# CORROSION FATIGUE

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# CORROSION FATIGUE

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# INTRODUCTION

Corrosion fatigue is a common occurrence. Yet, the process of neither the corrosion nor the fatigue is understood to the point where performance of a metal in a specific environment can be predicted without some sort of laboratory test.

In this thesis, one aspect of this complex process will be investigated that is; the role of microstress buildup within the metal. Specifically, the effect that these microstresses have on the corrosion rate is what is sought.

There is much that is unknown about microstress. A definition of the term is a formidable task. A true concept of microstress may help bridge the gap between the binding energy within the nucleus of an atom and the forces of attraction between the molecules in a crystal lattice. The concept of energy storage in metals is fairly recent and it seems to be a step in the direction of explaining these phenomena.

The problem is one of sizable magnitude. It is realized by the author that the possibility of a complete answer to this problem is remote.

However, if new light can be shed on this problem, if a different concept or approach can be devised, the value

of this thesis will be established. If not, its value will be in the added insight the author attained through dealing with some of the difficult problems in basic research.

## CHAPTER I

## CORROSION FATIGUE - GENERAL

The literature generally defines corrosion fatigue as the simultaneous action of corrosion and cyclic loading. The nature of neither the corroding action, nor the fatiguing action are completely understood, and, as would be expected, the theory falls short of explaining the experimental results, and results observed in actual practice.

### THE WORK OF GOUGH

Gough, who did a vast amount on the subject of corrosion fatigue publishing about 18 papers during the period 1926-1946, is careful in his definition of corrosion fatigue to avoid the use of corrosive environment, since he showed that some environments which would normally be considered corrosive had little or no effect on fatigue behavior, whereas others which would not normally be considered corrosive (e.g. air) had definite effects. He thus, in his definition defined the environment as one of an "oxidizing nature."[37] The importance of oxygen was emphasized because various investigations had shown that environments that would normally be considered corrosive did not produce corrosion fatigue when oxygen was absent.[37] This is readily understood when considering the corrosion as an electro chemical [redacted] mechanism. Since the cathodic reaction is the reduction of

dissolved oxygen, the supply of oxygen to the specimen surface may be a factor in controlling the rate of reaction. However, before it can definitely be stated as the controlling reaction (i.e. the reaction rate is the slowest), a study must be made of the kinetics of the reactions.

It is possible to conceive of corrosion fatigue occurring in the absence of oxygen where the cathodic reaction is the evolution of Hydrogen. Experiments by Evans and Simnad[53] on the corrosion fatigue of steel in acid solutions are examples of this.

Thus the term corrosion fatigue as used in this thesis refers to the simultaneous actions of cyclic stressing, and a corrosive environment. A corrosive environment is one in which corrosion takes place.

## CORROSION FATIGUE - STRESS CORROSION DEFINED

Perhaps at this time it might be well to differentiate between corrosion fatigue and stress corrosion as used in this thesis. In 1945, Sutton, Liddiard, Chalmers, and Champion proposed the following definition which has been widely accepted in the United States. "The term stress corrosion implies a greater deterioration in the mechanical properties of the material through the simultaneous action of <u>static</u> stress and exposure to corrosive environment than would occur by the separate but additive action of these agencies."[37] A definition of corrosion fatigue would be very similar with the only difference being that the

stress would be cyclic instead of static.

The damage from corrosion fatigue is greater than the sum of the damage arising from cyclic stresses and that due to corrosion.[81]

It is not strange that some of the literature considers laboratory scale fatigue tests to be "an expensive waste of time".[80] Indeed the establishment of any type of endurance limit for engineering design purposes would be nearly worthless.[82] The decrease in fatigue strength will depend on the amount of corrosion. In the simultaneous reaction of corrosion and fatigue, the corroding medium, the frequency of the cyclic loading, the stress, the temperature, etc. would all have some effect on the reaction taking place. It seems unlikely that complete duplication of inservice conditions would be accomplished, and extrapolation of experimental data can be dangerous.

## THE MECHANISM OF CORROSION FATIGUE FAILURE

The mechanism of failure by corrosion fatigue is explained by Uhlig.[81] This process is comprised of two stages. During the first stage, the combined action of corrosion and cyclic stresses damages the metal by pitting and crack formation, to such a degree that fracture by cyclic stressing would occur ultimately, even if the corrosive environment were removed.

The second stage,[81] explains Uhlig, is essentially a fatigue stage in which failure proceeds from cracks caused by the stress concentrations formed by the mechanically or chemically formed knotches. The mechanism is identical with failure by fatigue with the corrosive medium providing a source of stress raisers. The pitting and cracks could be caused by local anodic areas formed by either breaks in a built up oxide coating which is cathodic with respect to the base metal,[26] or possibly by differences in electro potential of different crystals or different faces of the same crystal caused by internal stresses built up during the fatigue process which could decrease the entropy, thus increase free energy of the system.

The fatigue process as described by Uhlig is also brought out clearly in Reference 71, but some of the more recent texts emphasize the role of internal stresses more.[75]

The role of the microstresses will be covered in Chapter II.

## PREDICTING CORROSION FATIGUE

In dealing with primarily ferrous metals, the resistance to corrosion fatigue is fairly predictable. That is, the alloys most susceptable to corrosion damage will have

the lowest corrosion fatigue resistance. A corollary to this is that maximum resistance to corrosion fatigue will be exhibited when the alloy is in the best condition to resist corrosion. Thus, high strength steels have a corrosion resistance close to that of plain mild steel. When alloying changes the metal's corrosion properties a change in corrosion fatigue[82] resistance is realized. High chromium steels, which have improved corrosion resistance, have improved resistance to corrosion fatigue.

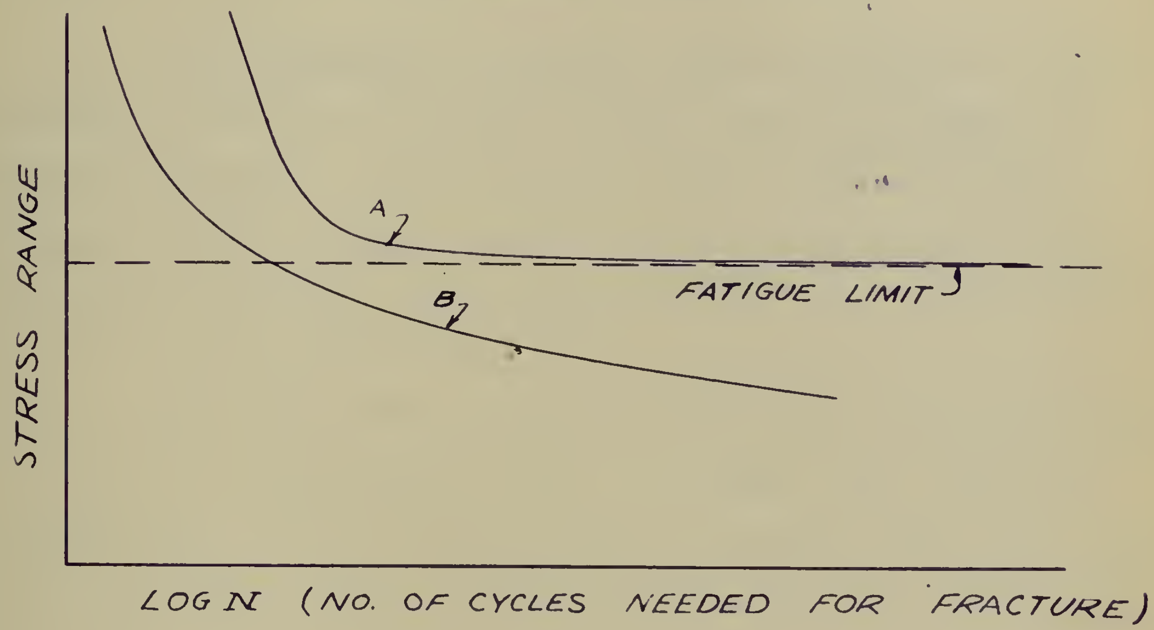
The literature does not really differentiate between failure by fatigue, and failure by corrosion fatigue, except that the latter is invariably faster.

It is difficult to distinguish between fatigue and corrosion fatigue. In actual practice, pure fatigue rarely exists. Fatigue tests in a vacuum give different results than fatigue tests in air, the former indicating considerably greater fatigue strength.[37, 57] Thus, fatigue and corrosion fatigue cannot in fact be regarded as distinct groups of phenomena. If the term fatigue be restricted to the fracture of metals under alternating stress in an environment devoid of corrosive substances, then it is doubtful if any real fatigue tests have been made.[37] Generally however, tests carried out in air are called fatigue tests.

The term fatigue strength has been referred to. In many respects, this particular mechanical property of a metal can be as elusive as its "yield strength." For some metals

it can be seen readily on a S/N curve of the usual form.

DRAWING ~ S/N CURVES




Note that curve A approaches asymptotically a limiting value of stress, and for stress below this value there will be no failure no matter how prolonged the test. In some cases (curve B) the curve does not become asymtotic to any particular stress level even after a very large number of cycles. In such cases, it is frequently convenient to speak of an endurance limit (N) which is a value of S just insufficient to produce fracture after N cycles. As was mentioned before, in the case where the corrosive atmosphere is highly oxidizing, any values of fatigue strength or endurance limit have very little meaning, and are of little practical engineer-

ing value. The above figure may be somewhat misleading in the fact that the knee of the curve looks fairly well defined. Actually, this point may vary by ± 20%.[117]

The mechanism of failure, which is unknown in many respects, seems to be the same in the cases of fatigue and corrosion fatigue. At any rate, in both cases the cracks propagate alone a transcrystalline path predominately, rather than in an intercrystalline manner.[46, 81.]

But, it is not possible to generalize with any accuracy. It is an oversimplification to suggest that corrosion fatigue always produces transgranular cracking, and that stress corrosion always produces intergranular cracks. In magnesium based alloys, corrosion fatigue produces intergranular cracks.[57]

The most important distinction is that corrosion fatigue can produce damage with any combination of material, heat-treatment, and corrosive agent whereas stress corrosion cracking occurs only after certain unfortunate combinations of these three factors.

## SOME EXPERIMENTS IN CORROSION FATIGUE

In the corrosion fatigue of a single crystal of aluminum under cyclic torsion stresses,[51] the general surface pitting bore no relation to the applied stress, however,

preferential corrosion occurred along the slip planes, this being the essential cause of failure. The distorted metal being anodic with respect to the base metal caused this localized corrosion. This factor is evident in cold worked steels. Their fatigue resistance is high due to the internal stresses, but they are particularly susceptable to corrosion fatigue.

In another experiment an aluminum specimen consisting of two crystals separated by an irregular boundary was subjected to six weeks of torsional stress under a slow stream of tap water. The boundary was not attacked by the corrosive medium. Failure occurred because of the formation of cracks in areas undergoing heavy plastic deformation.[116]

The failure by fatigue in the corrosion fatigue (the literature makes no distinction) of ductile metals is associated with failure of elasticity by slip. X-ray analysis has proved that the structure is fragmented into crystallites at slip planes, and it is probable that fatigue failure originates at local junctions of the crystallites where some lattice bonds rupture under continued stressing. Local strains are high at such points and bear no relation to average stress.[51] Thus, although the average stress may be well below the elastic limit, local stresses may easily approach the elastic limit. Fatigue failure is a consequence of the localized slip deformation which occurs within the individual crystals of metals.[130]

Fatigue can be described as a nucleation and growth process. The individual points of a metal differ in crystal perfection and orientation, microstructure, distribution of segregate and inclusions, microstress, etc. Therefore at some points a crack may be nucleated at low stresses while at others, higher stresses may be required.

The term "crystallites" used in the preceeding paragraphs has come under bombardment in more recent texts on metallurgy.[80, 87] Frequently the term may refer to a type of failure e.g. a metal crankshaft failed in service because it "crystallized." The implication is that service loads - usually at or only slightly above atmospheric temperatures -- have somehow caused very large crystals and therefore very weak crystals to grow locally in the metal. Presumably the weak region of coarse crystallization grows until the remaining unaltered section then fails in a brittle manner.[80] This type of description results primarily from observation of actual fatigue failure.

To the metallurgist, failure by "crystallization" is incredible since formation of large crystals in a solid metal simply does not occur at atmospheric temperatures within any finite period of time.[80]

In way of clarification, fatigue failure as it will be used in this thesis is fracture produced by cracking formed

and propagated by cyclic stressing below the elastic limit. The distinctive feature of the fatigue phenomenon is that very little measurable permanant set takes place prior to the brittle fracture.

A predicted quantitative correlation between fatigue and creep is found to exist in the case of annealed solutions.[67] This suggests the practical possibility of obtaining fatigue data for annealed solid solutions from steady state creep rate data for these materials. The phenomena of plastic deformation and fatigue are related, but the relation is not a simple one. Fatigue failure is usually associated with the propagation of a crack. This assumes that submicroscopic cracks do exist. Some experimenters have tried to explain fatigue on the theory of dislocation.[67] They haven't been too successful.

## THE WORK OF McADAMS

A substantial amount of work was done by McAdams[21, 26] in the area of corrosion fatigue in the time period 1926-1941. He performed a variety of fatigue test mostly of the simultanious fatigue and corrosion action, however, he also performed a series of tests, corroding first, then fatiguing. In the latter tests, the decrease in the fatigue limit was used to measure the damage resulting from prior corrosion. McAdams introduced the term corrosion fatigue.[37]

McAdams found that the greater the stress, cycle frequency, and time in the corrosion stage, the greater is the difference between the resultant damage and the corresponding

damage caused when the material is in the unstressed condition.[26] The difference, McAdams defines as the net damage which he considers a measure of the influence of cyclic stress on corrosion.[26] It may be difficult to argue with his definition, but the results obtained from his experiments, especially those of net damage seem of little practical engineering value.

At any rate, fatigue seems to be a race between hardening and damage. The larger the strain per cycle, the greater the damage relative to the increase in hardness, and the sooner failure occurs.[15]

## RECENT EXPERIMENTS IN CORROSION FATIGUE

Some recent investigators have tried to relate changes in other mechanical properties after the specimen had been fatigued. This type of research had often been done with irradiated specimens also. One of the major objections with this type of approach is that bulk measurements on fatigued specimens, most frequently, cannot be sensitive to the changes produced by cyclic stressing since such stresses localize their effect in small areas, such as metallurgical notches and other defects that act as stress concentrations.

Reference 126 contains an interesting series of experiments where tensile and Charpy Vee-notch specimens were made from the fatigue specimen after cycling was completed.

Different grain sizes were used. The grain size was controlled by heating the metal until recrystallization and subsequent grain growth took place. In this group of experiments, the bulk measurements of yield stress and fracture stress were considered to reflect the structural changes brought about by fatigue.

The fatigue hardened structure can exert a powerful locking action on the dislocations.[126] Plastic deformation releases the existing dislocations from a random network into a more ordered form. This process indicates a decrease in entropy. It would then follow that a decrease in entropy would increase the free energy of the metal in solution, thus, the chemical properties would be altered. (See Appendix)

The history of a metal, if known, may play a very important part in predicting its behavior under fatigue conditions.[114] Cyclic stressing may also be a means of stress relieving.[25, 57] In certain experiments[130] complete removal of strain hardening effects brought about by prior deformation were removed by additional cyclic strain. Residual stresses that result from dynamic loading may sometimes be reduced by cyclic loading with low stress at or near their resonant frequency by means of vibration generators.[25] Repeated slow loading at high stresses is sometimes used in order to produce a similar static effect. Care must be taken primarily with

the latter method, to avoid stresses that are too high, or too many repetitions of stress, since either might lead to fatigue failure.[25] The literature offers insufficient information and data to warrant the conclusion that cyclic stressing is a satisfactory means of stress relief, but there is much in practical experience to support this belief. Many formed plates in ship structure that had to be forced to fit, perhaps with great difficulty, can later be removed and replaced with ease. It is true that all of the residual stresses are not relieved, however, the peak stresses have been relieved since the plates retain their original shape. It is probable that stress relief took place only in those places where the stress was sufficiently high to cause plastic flow.[25]

Under cyclic strain conditions, some materials will strain harden, while other materials, particularly cold worked structures, strain soften.[130] This leads logically to the conclusion concerning fatigue that, as in all other mechanical properties of metals, the structure of the metal has a profound influence on its cyclic strain behavior.

The grain size of a metal affects such mechanical properties as tensile and creep strength, however, it has little or no effect upon the strain fatigue resistance of certain metals, such as 347 stainless steel.[133] But, generalizations once again can lead to erroneous conclusions. In plate material, the large grain size material had a higher

fatigue strength than small grain size material. In bar stock specimens, the reverse is true.[133]

The effect of a near saturation unidirectional magnetic field was to decrease slightly the endurance life in Armco iron in the annealed condition.[132] This might be predictable since the energy absorbing mechanism associated with domain movement is inhibited by the strong field. That is, the anisotropic energy tends to orient domains along certain directions of easy magnetism. The applied field tends to make the domains grow that are favorably oriented with respect to the field. The orientation caused by the field would upset the natural orientation of the crystal which is resisting the cyclic strain. As regards the above mentioned domain structure, the theory of the microscopic behavior of ferromagnetic and ferroelectric crystals depends on their consisting of large numbers of domains, each polarized to saturation, but pointing in different directions so as to minimize the energy.

One of the properties of a metal which might be thought to influence fatigue life is its damping capacity.[132] There are two major groups of mechanisms which provide damping at a stress level where fatigue failure becomes possible:

1. magnetic damping (hysteresis and eddy current)

2. plastic hysteresis (dislocation damping and viscous behavior at incoherent boundaries)

At low stresses (below the endurance limit) the magnitude of magnetic hysteresis is large[redacted] compared with plastic hysteresis. Note that damping capacity is not necessarily the algebraic sum of the results of individual mechanisms. If magnetic damping is inhibited, the remaining mechanisms may operate more or less effectively than formerly.[132] The interaction of these two mechanisms is a complicated matter. This is, in effect, an alternating domain pattern under the influence of repeated stress. Experimentally, it has proved difficult to predict stress. It may be unrealistic from the practical standpoint of fatigue problems.

A literature search was made into this particular area in connection with the laboratory part of this thesis. It was thought that fatigue introduced by using the property of magneto-striction which some metals (e.g. nickel, and iron, although iron to a lesser amount) possess, could be more accurately controlled, thus allowing greater repeatability. The use of a higher frequency of cycling could be used, thus the time required for a series of laboratory experiments would be reduced. The complex mixture of magnetic and plastic cycling led to the rejection of this method as a means of introducing residual stress. More will be said about this in the chapter on microstresses.

## GENERAL THEORIES CONCERNING FATIGUE AND CORROSION FATIGUE

As was mentioned before, the theories in existence

fall short of explaining physical phenomena. This may be because of our mathematical model. It may be too simple in its orderly representation of crystal lattice, although it seems fairly good in some respects.

There has been over the years, a development of theories concerning fatigue which help to answer some of the phenomena observed in experiments, and in actual practice. These have attempted to deal with some of the striking features or phenomena of the fatigue processes. Some of these features are as follows:[65]

1. Quasi-brittle nature of fatigue fracture i.e. ductile metals can break in a fatigue test without any appreciable external deformation.

2. Heavy local distortion can be observed microscopically and also shown by X-rays.

3. There are "safe ranges."

The attrition theory, credited to Ewing and Humfrey was based on the observation of the microscopic slip mentioned. This assumed that the slipping surfaces (plastic deformation taking place) became increasingly abraded, and their cohesion diminishes until finally a crack appears.[65]

Gough and Hanson recognized the fundamental role played by plastic inhomogeneities in fatigue as well as elastic

recovery and hysteresis. They emphasized that the plastic regions of plastically inhomogeneous material can become strain hardened by alternating stresses without any external strain being produced. The blurring of X-ray photographs in the course of the fatigue test would correspond to a progressive break up of the crystal into small fragments. The fragmentation would diminish the cohesion, and a crack would develop.[65]

Orowan's ideas bring the state of the theory a little further along. He states that[65] the unavoidable presence of small cracks and structural inhomogeities causes the stress distribution to be inhomogeneous in all materials. If the material is brittle, the fracture occurs when the stress at the point where the stress concentration is the highest reaches the value of the stress needed to produce fracture.

Plastic material yields at stress peaks before fracture occurs i.e. increase in load increases plastic strain and, with cyclic loading, progressive strain hardening is produced.[65]

Note that this "plastic inhomogeneity" need not be a fault in the ordinary metallurgical sense, but may be merely a crystallite oriented unfavorably with respect to the applied stress so that its yield point is exceeded by a load that produces only elastic strains in the surrounding metal.[71]

These localized inhomogeneities may be expected in any polycrystalline metal, and even in single crystals. Orowan considers in some detail the effects of repeated loading on a simplified model containing a plastic inhomogeneity within elastic surroundings. He found that successive plastic deformation under each cycle of stressing of the small region causes two effects: (1) Deformation which may be cumulative under succeeding cycles until a self propagating crack is formed, and (2) local strain hardening and corresponding stress relief which strengthens the region and shifts stress maxima under succeeding cycles to adjacent portions. Orowan, making particular simplifying assumptions concerning these effects, was able to explain semi quantitatively, many of the observed phenomena of fatigue behavior of metals.[71]

Some of the more recent authors indicate that statistical theory in the fatigue of metals is a truer representation than any of the previous theories. As was mentioned before, endurance limits may easily differ by $\pm$ 20%, thus the endurance limit is looked upon as a statistical quantity and therefore should be determined by statistical means. But, once again, simplifying assumptions must be made, one of the usual ones being isotropy.[68]

Since there are many factors which effect the fatigue resistance in materials that are random (e.g. lattice defects, crystal orientation, to mention two) it would be expected that a statistical analysis might provide a logical approach. Some

have been attempted.[68, 117] Fatigue performance is represented by a three dimensional S-N-P relationship.

Where: S = Stress amplitude

N = Number of cycles

P = Probability of failure at any number of cycles $\leqq N$ $0<P<1$

Data from S-N diagrams established by conventional procedure provides, at best, a rough indication of the trend of the S-N relations within an undefined, broad range of probability values.[117] In these analyses, many specimens are used, especially near the "knee" of the S-N curve.

The work in the literature is too extensive to be detailed in a thesis of this sort. The need for a new approach is evident since there has been virtually no change in the reporting of fatigue data in 20 years. There is much data available, but no method of correlation. Statistical theories answer some of the problems within certain probability limits which are established using many specimens. The size effect, previously mentioned, cannot be predicted by theory.[117]

Stress concentration factors must be utilized in the statistical process. In actual practice, the stress concentration factors are less than the theoretical or geometric stress concentration factors as calculated by the classical theory of elasticity. Note: the theoretical stress concentration factor is the ratio of the maximum theoretical stress

at the notch or stress raiser to the nominal stress which would be present without the influence of the notch or stress raiser. The maximum theoretical stress is obtained from the theory of elasticity or by photo elastic tests. These factors seem to widen the breach between a theoretical and experimental analysis.

## CLOSURE

The purpose of the first chapter in this thesis is to emphasize the complexity of the subject. It is by no means considered sufficiently covered, however it is considered that an adequate search was made into the literature to discern areas where valid conclusions cannot be drawn due to lack of evidence. It also served a purpose in the definition of terms. In the literature, the term corrosion fatigue does not refer to any one particular phenomenon.

The author does not agree with some modern authors that "laboratory tests are an expensive waste of time".[80] Laboratory tests, in this field, have been able to expose the many facets of the process. The theories lag far behind in explaining the results of laboratory tests. Experimental results have provided the design engineer with usable data. To be sure, fairly wide margins are applied to this data. In practical engineering, the theory, thus far has been unusable.

If any major progression is to be made on this subject, it will probably come from theoretical analysis. In the

interim time, laboratory work will produce the results which the theorist must seek to explain. In this light, laboratory work is discussed, and some experiments attempting to relate cause and effect are submitted.

# CHAPTER II

## MICROSTRESSES AND THEIR MEASUREMENT

Any chapter on microstresses perhaps should start with a definition. This may prove to be quite a task since the variance in definitions is almost as great as the reference books containing information about them. In many cases they are called by various names i.e. internal stress, residual stress, locked up stress, etc.

## THE WORK OF LASZLO

Perhaps the classic work done in this particular area was done by Laszlo in his 5 part series on Tessellated Stresses.[1] He calls the internal stresses caused by external loads "body stresses," and he defines the tessellated stresses as internal, self compensating stresses which depend on the orientation of the neighboring crystal and therefore involve probability in determination. (i.e. it can be determined that they lie between certain maximum and minimum values, depending on the space configuration.)

These tessellated stresses also develop in solids that consist of, or transform into, components which have different physical properties. These, Laszlo refers to as structural tessellated stresses to distinguish from stresses due to anisotropy. (condition of exhibiting directional

properties in this case, as related to stress.)

In general, tessellated stresses form three dimensional systems and their investigation by direct measurement would be difficult.

E. Orowan[9] divides the internal stresses into two categories:

1. Body stresses (usually macroscopic) arising from non uniformity of external (mechanical, thermal, or chemical) influence acting upon the body.

2. Textural stresses (usually microscopic) due to textural inhomogeneities which may be present in the material internally, or produced by plastic deformation or structural change.

## MICRO AND MACRO STRESSES AS TERMS

The terms micro and macroscopic can be misleading. The residual stress left behind after plastic deformation in a microscopically small volume at the bottom of a sharp notch would be classified as a macrostress or body stress as Laszlo defines it, while a large scale internal stress

due to the mutual interference of two large grains in a strained bi-crystal is termed a microstress even though the length over which the stress acts may measure in inches.

More recent definitions [25] define microstresses as stresses which act over distances of the order of magnitude of grain diameters. These are also known as Heyn stresses. Residual stresses caused by differential plastic flow resulting from rapid and uneven cooling of hot metal or from mechanical loading or working, are usually distributed through appreciable volumes and are referred to as "macrostresses." Also, residual stresses accompanying phase transformations are usually distributed through microscopic volumes only, and are called "microstresses."

Unfortunately most microstresses cannot be controlled since they are usually of unknown magnitude and random orientation. They are, however, in equilibrium and thus must balance each other.

A. S. M. E. in their Metals Engineering handbook [82] define macrostresses as stresses distributed uniformly over appreciable areas. Microstresses are stresses which vary from grain to grain or with a grain..

Macrostresses, sometimes referred to as body

stresses of the first order, are generally determined quantitatively and evaluated in terms of performance of manufactured products. The exact influence of micro-stresses is not understood, but they have some relation to the processes of age hardening, precipitation, diffusion in alloys,[82] strain hardening, recrystallization, grain growth, and creep effects.

Theoretically, there are no micro or macro stresses. There is only one kind of stress. The stress at a point is a tensor, and a point is neither macro or micro.[101, 139] Residual stresses in a body are caused by some sort of misfit between its various parts, i.e. crystals. Differential expansion may also be caused by a metal at an elevated temperature being allowed to cool to room temperature. The differential expansion of the grains sets up stresses from grain to grain which may be of very high magnitude, but balanced withwa very local region.

Practically all metal crystals are elastically anisotropic, thus, Young's modulus is different in different directions. So it seems that if a single phase polycrystalline metal with a random grain orientation is subjected to a uniform load, neither the stresses nor the strains in the individual grains will be the same, and a system of microstresses result. In a two phase metal, the

crystals do not need to be anisotropic provided the two phases have different elastic constants, in order to produce a similar microstress system.[101] Plastic deformation of crystals is a highly anisotropic process, and since it is irreversible, the resultant microstress system is residual in nature. Phase changes that result in volume changes also produce a system of microstresses.

It seems no firm definition can be formed from the literature. Indeed it seems that where particular phenomena are being described, a definition must accompany the terms used.

From the metallurgical standpoint, great interest attaches to the determination of the cohesive forces in a metal binding the structure together. It is unfortunately not possible at present to relate the cohesive forces of a metal to its structural and mechanical properties.[88]

It is in this area where perhaps a true definition of microstresses or the stresses which produce the phenomena generally attributed to microstresses might evolve.

In this thesis, a definition of microstresses, residual, locked up stresses (synonymous terms all referring to the same phenomenon) will be developed. It will be per-

haps a little unconventional when compared with the major portion of the experimental work done a few years previous, but it will be more in line with more current thinking. The development of this definition has come from literature searches and the authors' attempts at developing a method of measuring these microstresses, and of determining the effect that microstresses have on other properties in particular, corrosion fatigue of the metal. A brief survey of the nature of microstresses follows.

There are certain particular problems in understanding the role of residual stresses.

1. They are difficult to isolate per se because such stresses are usually accompanied by some kind of structural or phase change in the material.

2. Superposition of the residual stress pattern on the stress system arising from any external loading system is not clearly understood in relation to fatigue strength.

3. There are no generally known means where residual stresses can be accurately measured.

4. Residual stresses also depend upon previous history, so that they change, fade out, or even go from compression into tension and vice versa, as a result of cyclic loading.

5. Crystal orientation also affects the residual stresses. This point may be turned around to state that residual stresses affect crystal orientation with equal truth as regards to the present boundaries of knowledge of this subject as reflected in the literature.

Never-the-less, some attempts have been made to determine these residual stresses. An interesting mechanical method is recorded in reference 15.

## MECHANICAL METHODS OF MEASURING RESIDUAL STRESSES

Briefly, a slug of metal was cut from the center region of a forging so that it would be outside the region of the wheel fit. SR 4 gages were cemented to the outside diameter of the slug at four locations spaced $90^o$ apart. Each gage measured strain in the longitudinal and tangential directions.

The magnitude and distribution of residual stresses were determined by measuring the relief of strain after each successive boring out operation, and supplemented by a final operation on the remaining thin shell of slitting and cutting small strips.

By this method, a linear stress distribution is assumed through the wall section. (Note: they are dealing with hollow cylinders). This assumption is probably a fair approximation for certain cases. However, for flame hardened or surface rolled specimen some valid doubt as to this linear assumption is warrented.

This method does have some serious draw backs. It is difficult to remove a uniform layer, also, the process itself introduces residual stress both by abrasion, and thermal effects. It is questionable whether the assumption of proportionality between the residual stresses relieved by cutting and the elastic deformation measured is valid.[139]

Reference 15 contained plots of stress vs. radial location for specific cases. They are a matter of academic interest, but once again, of little use to the designer.

Residual surface stresses caused by shot peening or grinding may improve the fatigue resistance of a metal. However, there are many variables. Studies have been made

with hardened steel in an attempt to correlate the fatigue limit with residual stresses generated in flat bar tests by longitudinal surface grinding. Reversed bending fatigue tests showed that for good commercial grinding conditions, the fatigue limit was the same when unstressed by grinding, and when "gentle" grinding technique was utilized. Severe grinding caused a decrease in the fatigue limit of about 13%.[135] With other specimens, an increase in the fatigue limit up to 38% were experienced.

In the grinding process, three general types of stress distributions were found for the grinding condition utilized. The distinguishing feature of these stress patterns are:[135]

1. The residual stress is tensile at the surface. The peak tensile stress may occur slightly subsurface.

2. The residual stress is compressive at the surface. A significant peak stress occurs slightly subsurface.

3. The residual stress is compressive at the surface. Either a small

peak tensile stress (less than 5000 p.s.i.) occurs slightly sub-surface, or no significant sub-surface tensile peak is observed.

The stress patterns described resulted solely from the test grinding operation, and did not contain any components ascribable to the previous operation in which the test bars had been ground to the intermediate thickness of .140 135 inch~~es~~.

The residual stresses were determined by the deflection method, using a comparator based on the differential transformer principle. The curvature parallel and perpendicular to the direction of grinding were measured. This direction was also the direction of principle stresses. Measurements were taken as successive uniform layers were removed from the surface of the specimen.

A jig is used to position the specimen. Three vertical posts, two of which contact the specimens edges determine the reference plane. The curvature along lines through the midpoint of the specimen parallel and perpendicular to the direction of abrasive travel were determined from the displacement of the midpoint of the reference surface with respect to a straight line joining its points of contact.

In this series of experiments, each value of curvature used in plotting working curves for calculating stresses was the average of five separate comparisons of the test specimen with a standard known flatness.[136]

It is interesting to note that the stress distribution was found to be nearly the same in both the directions, parallel to, and perpendicular to the direction of grinding. The principal difference was that the perpendicular tensile stresses were always somewhat lower algebraically than the parallel ones. Thus the perpendicular tensile stresses were smaller and the compressive stresses were larger. The compressive stresses could be neglected since it was found that the maximum tensile stress appeared to be the controlling factor with respect to fatigue properties.[135] It was also found that cyclic stressing did not affect the shape of the stress distribution curves.

There was appreciable scatter in the results of the experiments mentioned in the few preceeding paragraphs. Much of the more recent literature notes the influence of inclusions and defects in engineering materials on scatter in fatigue tests. These series of experiments bear out that metallurgical discontinuities are important in this regard.

On the basis of these experiments, [135] some general beliefs regarding surface residual stress and fatigue were offered.

1. Surface tensile residual stresses decrease fatigue strength.

2. Surface compressive residual stresses increase fatigue strength.

Surface stresses alone whether compressive or tensile are not sufficient to determine whether improvement or reduction in fatigue strength will occur.

Residual stress patterns produced by grinding have also been studied by means of X-ray diffraction and optical interferometer methods. Results of these methods indicate that light grinding produced residual compressive stress. Heavy grinding produced residual tensile stress. [138]

## X-RAY METHODS

As is known, crystalline materials have regular atomic structure in which the atom spacing is changed by elastic stress, but not by plastic deformation. [82] The wavelength of an x-ray beam is of about the same order as the atomic spacing so that it offers a convenient means

of measuring any change resulting from stress. Once again this is a qualatative process since due to the anisotropy of the material the true direction of stress may not be known. Further, the problem is three dimentional thus with any photograph, strain in only one plane can be determined.

This form of testing has the advantage over mechanical tests in that it is non destructive. X-ray diffraction also allows determination over a small area where stress concentrations or steep stress gradients are present.[82]

Some disadvantages are that x-ray diffraction will measure only elastic deformation of thin specimens, since the beam has little penetration into the interior. Up to the present time, it has only been satisfactory for metals yielding reasonably sharp diffraction lines.

X-rays used in stress measurement penetrate but a few thousandths of an inch at most into the metal specimens.[105] The preparation of the surface is a highly important factor in the process. Electropolishing is preferable to etching since the effect of etch pits, even if quite fine may give erroneous readings. (i.e. the metal just under the surface may exhibit higher stresses.) This type of measurement has been used for shot peened, and ground specimens.[105] An important characteristic is that x-rays measure only

elastic components of strain, not plastic. Currently, the accuracy of the x-ray diffraction method is ± 5000 p.s.i. in hardened metal and ± 3000 p.s.i. in annealed specimens. The difference in accuracy between the annealed and hardened specimen results from the plastic deformation which has taken place in the hardened specimen. This results in "fuzzy" photographs.

## ELECTRICAL AND MAGNETIC METHODS

Stresses in wires and other small specimens of measurable resistance, have been measured by changes in conductivity with changes in applied stress. Theory indicates that a perfectly periodic metallic crystal lattice has perfect conductivity, that is, zero electrical resistance.[112]

Magnetic methods are sometimes used to determine fatigue damage, and direction and relative magnitude of residual stress. An example of this is the cyclograph which measures, on a relative basis, the hysteresis and eddy current losses set up by the insertion of a metallic core in a high frequency coil which is supplied with current from a highly sensitive oscillator. The influence of changes in the crystal structure of the coil due to stresses has the effect of changing the coil field intensity and output of the oscillator.[79] Note that eddy current

losses and hysteresis losses could not be separated. As the stress increases, these losses increase also. Measurements of these types are made while the metal is being stressed. The residual stress are isolated from the dynamic loading by periodic investigation of the material when entierely free of external load.[79]

## CALORIMETRY AND DIFFERENTIAL TEMPERATURE MEASUREMENT

Annealing is a means of stress relief. Thus it would seem that if a means could be devised to measure the amount of energy relieved in the annealing process that this could be correlated to the residual stress in the metal.

Measurements similar to this type were made in a calorimeter. Thus, if a plot of heat evolution vs. temperature were made, peaks would occur where recrystallization and thus relief of stress occurred.[140] Some authors concluded that all stored energy was released before crystallization.[141] The stored energy of cold work is small compared with heat effects usually measured. For example, a typical metal stores energy of the order of only 1 percent of its heat of fusion.[140] Thus the measurement of this energy release presents considerable experimental problems. There has been a variety of methods applied throughout the years, but they fall generally into two categories:

1. Single step methods in which all measurements are made during the deformation.

2. Two-step methods in which the deformation is carried out first and the stored energy measured at a later time.[140]

A similar experiment using a differential thermocouple was being devised by the author. In this type of experiment, the differential thermocouple would be attached to an annealed specimen and a similar specimen that was subjected to cyclic stressing. The two specimens would then be placed in a furnace and annealed. The differential thermocouple would measure the difference in temperature of the two specimens. This difference should be zero except when internal energy is released. Peaks in a curve should appear at these points. The possibility of relating these peaks temperature difference to internal stress was considered.

Perhaps a bit prematurely, the concept of residual stress as stored energy is introduced. This will be covered more completely further in this chapter under "MICROSTRESSES AND LATENT ENERGY - A Definition."

## SOME CAUSES OF MICROSTRESSES

The causes of residual stresses are many. Thermal expansion, phase change, diffusion, and magnetostriction may cause the specific volume to undergo change. Internal stresses usually accompany these phenomena. Uniformity is a factor, however. If the above mentioned processes take place with perfect uniformity throughout the body, internal stresses would probably not result. This is true also for plastic deformation. If plastic deformation takes place in a very localized area, high internal stresses may result. Microstresses cannot exist in an isotropic, homogeneous medium. These mediums rarely exist.

The fact that thermal expansion can cause internal stresses may cause some question, since one of the more common means of stress relief is heating. However, stressed metal, when heated, can crack.[113] Even though heating can relieve internal stress, it takes a finite length of time to accomplish it. The thermal stress and residual stresses acting together can cause the stresses to exceed the fracture stress.[113] It must be remembered that the initiation of fracture is a very localized effect.[101]

## CLASSIFICATION OF RESIDUAL STRESSES

Residual stresses can be classified as to their origin. (i.e. they are residual after what?) These stresses

can be caused by such processes as solidification and subsequent cooling, non uniform geometry changes, inhomogeneous volume changes, etc. Perhaps one of the more interesting is the transformation microstresses associated with steels. When cooling is too rapid to permit the migration of carbon atoms to form $Fe_3C$, the transformation from austenite to ferrite is interfered with and the tetragonal martensite lattice results. The shear transformation to a martensite plate produces in the surrounding matrix residual shear stresses which oppose further transformation. Hence the amount of martensite produced at a given temperature is limited by the balance between the elastic strain energy stored in the austenite matrix and its instability in the form of free energy. Since the latter increases with decreasing temperature, the relative amount of martensite obtained increases as the temperature is lowered.[112]

## MICROSTRESSES AND FATIGUE

A true theory of fatigue is lacking. The role of the microstresses in fatigue is unknown. The accepted conclusion generally in the literature is that residual stresses do affect the fatigue strength in that they super impose with other stresses.[101] This point is refuted by some more recent literature. Reference 139 states that the law of superposition is not valid because of the inter-

vention of plastic deformation. It is known that residual stresses can disappear after quite minor plastic deformation has taken place. There is fairly general agreement, however, that surface stresses, whether tensile or compressive in a material having a yield point may affect the apparent fatigue strength by something of the order of 10% at most.[101] Materials under conditions of reversed or rotating bending will, in general, not be affected by residual stresses to this extent.[101]

Residual stresses provide an internal balanced system of stresses produced by mutual interaction of various elements.[101, 139] From the standpoint of structural analysis, residual stress measurements have limited utility. First of all, residual stress cannot be determined to the same degree of accuracy as stresses due to loads. Even if residual stresses could be accurately determined, it cannot be assumed that they would exercise the same effect as stresses due to external loads.[139] The object of the engineer in determining stresses is to come up with adequate scantlings for a structure. Residual stresses are not effected by changes in dimensions as are load stresses. Load stresses can be limited by using a safety factor. Residual cannot be limited this way. In steel structures, where welding has been used, it is a safe assumption that at some

point in the metal, perhaps near the weld that the yield point of the material has been exceeded due to residual stresses.

One need only ask the question: "If the residual stresses in a welded ship were precisely known at every point both with regard to magnitude and direction, what could one do with such knowledge? How could he apply it practically? What conclusions could be drawn from it?" The answer would be: none whatsoever.[139]

The preceeding paragraph is a direct quotation from A.S.M. "Seminar on Residual Stress" November 1958. A practical engineer would agree wholeheartedly, since stress is to him, the criteria for scantlings. There are, however, many phenomena which a designer may not take into account in his calculations, that may be effected by residual stresses. For example: one may conclude that while residual stresses could not produce any reduction in the buckling load of a column as a whole, they can do so indirectly by precipitating local instability in the parts of which the column is composed. This possibility is supported by experimental evidence using rivited and welded box section columns.[139]

In the presence of residual stresses, local yield-

ing will occur at certain points in the structure earlier than it would in the absence of residual stress. This can be interpreted as a change in the stress-strain relation of the material. Any change in the stress-strain diagram will affect the buckling load.

The effect of residual stress on fatigue has been determined by a vast number of experiments, although the process is still not understood. Fatigue stresses may be superimposed on static residual stresses. The joint action is not understood.[139] Shot peening, surface rolling, and other cold work processes are known to produce increased fatigue strength.

In regards to failure in ship's plating, it is by no means clear that fatigue may not be a factor in the failure of welded ships. However, in spite of detailed examination of fractures, none of the fractures at the point of initiation have shown the typical characteristics usually associated with fatigue failure.[101] Residual stresses assist in the initiation of brittle fracture in ships and affect adversely the fatigue strength of ship steel. The effect of residual stress in the progagation of ship failure is less clear; but unless spontaneous fracture can be explained in the absence of residual stress, these stresses cannot be considered unimportant.[101]

All this is not to say that a more fruitful source of reducing ship fractures may not lie in improved steel or elsewhere than in going to great lengths to lower the residual stresses.[101] It may be that the presence of large amounts of latent energy in such structures as ships would be the largest single factor contributing to fracture.[101]

## MICROSTRESSES AND LATENT ENERGY

### A Definition

More often than not, there will be a connection between micro and body (or macro) stress distribution.[112] There is stored energy associated with every stress system. This stored energy can be calculated if the stress system is completely known. The problem is, of course, that the stress system is seldom completely known. The crystals, by forming a random configuration, are the complicating feature.

Internal stresses may also arise when a ferro magnetic material is placed in a magnetic field. These stresses result from the phenomenon of magnetostriction. This point was also discussed in Chapter I. These stresses result from an inhomogenity of deformation, both elastic and plastic, on a nearly submicroscopic scale.[112] Small regions (domains) of material have the electron spins ulti-

mately responsible for magnetic properties) aligned in common in a crystallographic direction so that each domain is magnetized to saturation in that direction. In the unmagnetized state, the domains have their various characteristic magnetic directions randomly distributed to effect zero net magnetization.[112]

When tension is applied to a specimen, the magnetization of the domain tends to become aligned parallel to the direction of the applied force. When compression is applied, the domain tends to align transversely.[112]

In magnetostriction then, an applied mechanical stress within the elastic range changes the permeability in the direction of the stress. Conversely, the magnetization of a material changes the dimensions in the direction of magnetization. A state of residual stress can resist additional strain from magnetization. That is, the residual stress present in a cold worked metal may oppose a change in magnetism. This is important since it indicates that the residual stress state requires and represents a storage of energy within the body.[112]

The activation energy required for a chemical reaction may be supplied in part by residual strain energy.[112] This is apparent in the microscopic examination of etched

metallographic specimens. Sites of locally higher strain energy, i.e. grain and twin boundaries and deformation markings are preferentially attacked. The free energy or chemical potential of these regions is also higher than those of lesser strain.[112]

Approaches to measure residual stresses for use in evaluating brittle fracture, creep effects, crack propagation, fatigue failure, stress corrosion, corrosion fatigue, and related fields have definite purposes in mind. Many of these experiments deal with some kind of internal energy build up. This latént or stored energy build up is thought to effect the previously mentioned phenomena. Efforts to measure this latent energy and to determine what its effect on mechanical properties have largely met with unsuccess. Most of the energy expended in deforming a metal is dissipated a heat. However, a small portion is stored in the metal.[121] At the present time, no satisfactory explanation has been given for the mechanism by which most of the mechanical energy is converted into heat.[121] The small portion of stored energy is of interest since it is postulated in this thesis that this energy (latent) can decrease the entropy that is the order of randomness of the metallurgical defects thus increase the free energy, thos making the metal, in general, more active chemically.

The reader may frequently get confused with the

variety of terms used such as: microstress, residual stress, locked up stress, etc. As was mentioned before, a definition that would conform to the literature is impossible since no clear definition exists. Indeed some definitions actually contradict each other. In this thesis, the terms microstress and residual stress will be used synonymously. They refer to internal stress which cause the latent energy build up of the metal and in this thesis, they are thus defined. The term latent energy infers the absence of structural stress (or body stresses as Laszlo calls them). Internal stress represents energy. The effect of this energy on corrosion fatigue is what is sought in this thesis.

The author has departed from many researches in this field in considering residual stress as an energy phenomenon. Previously it was convenient to think in terms of stress since if superposition with structural loads holds, straight addition of stresses may lead a number of solution the actual state of stress. There is serious doubt that superposition holds since residual stress is an internally balanced system of stress, and certainly changes in scantlings will have no effect on the magnitude of these stresses.

The definition of residual stress as a latent energy

phenomenon is convenient in this thesis since fracture stress is not sought, but rather changes in electrochemical behavior. This definition is also convenient since it includes phenomena indirectly related to stress, but difficult to attribute as a direct result. For example, the changes in crystal orientation and defect pattern under a stress system decreases the randomness, thus the entropy of the system. This change increases the free energy. (see appendix) The more ordered arrangement of the crystals may, in some metals, be accompanied by phase changes, thus changes in lattice structure. This change in lattice structure produces a metal with different mechanical properties. The direction of the change in mechanical properties is not always predictable since the phase changes differ in different metals. The effect of this latent energy is then a very <u>specific</u> effect, i.e. specific to a metal and its environment. It is difficult and dangerous to generalize the effect to many different metals.

The definition of residual stress as a latent energy phenomenon is convenient in other phases of mechanical testing. The rapid propagation of fracture (brittle or essentially brittle) is considered to be conditioned by the release of elastic energy from the system.[101] An interesting problem that has come to the author as a result of this literature search is the relation between notch sensitivity and

latent energy. Does notch sensitivity exist in annealed materials above the transition temperature? It is known that in the notch-brittle condition, i.e. below the transition temperature, brittle fracture can occur when residual stresses are present, and when they are not.[101]

Certain literature sources deal primarily with the dissipation of the mechanical energy of deformation. Aside from heat generated during deformation, dislocations seem to account for at least 10% of this dissipation.[121] Free energy is practically equal to the strain energy which is positive and large. Hence, dislocations cannot exist as thermodynamically stable lattice defects.[123] Four mechanisms for dissipating energy are considered to exist:[121]

1. The moving dislocation acquires a large kinetic energy that is released when the dislocation is stopped.

2. The dislocation dissipates energy continuously through thermoelastic damping, radiation damping and scattering of sound waves.

3. Large lengths of dislocation lines are created and annihilated during

the deformation.

4. Large number of point defects are created and annihilated during the deformation.

The first two possibilities have been considered in detail by various authors and found to provide inadequate dissipation of energy unless the dislocations are moving at speeds comparable to that of sound.[60, 121] The evidence is that dislocations do not move at such speeds. Also, no. 3 above accounts for only about 10% of the dissipated energy. The last conclusion would be modified if individual slip lines actually consisted of short lengths of line each length arising from a different dislocation. For slip lines to form in this way, the operating sources would have to be grouped together in neighboring planes. If this is true, the slip lines would each be at certain stages composed of short discrete lengths of line. This last effect has not been observed.[121]

The mechanism of the fourth possibility is interesting. The moving dislocations become jogged and thus create trails of point defects behind them during their further movement. Nearly all of these defects then disappear rapidly either by absorption at sinks or by recombin-

ation with other defects. Such recombinations may take the form of annihilations or the creation of clusters or stacking faults.[121] The conclusion of this analysis was that dislocations cannot account for the dissipation of energy during cold work at room temperatures. However, on theoretical grounds, sufficient point defects should be created to account for the dissipation provided they can subsequently cluster or annihilate each other.[121]

## CLOSURE

Internal energy build up can be caused by elastic deformation. However, when the loading is released, the internal energy resumes its previous level. Thus in the definition of microstresses as latent energy, it must be emphasized that this stored energy has not resulted from pure elastic deformation, since local yielding must have taken place for a residual stress system to result.

Microstress considered as latent energy also does away with the disturbing size dilemma. The terms micro and macro have no connotation. Its application is specific i.e. it must apply only to crystalline material. It may be difficult to perceive how residual stress could effect such processes as age hardening, recrystallization, grain growth, and other phenomena related to crystalline material. Considering these processes as ones which change the latent

energy level seems to the author at least, a more scientific approach. Efforts to correlate this latent energy with the thermodynamic properties of a metal seems worthwhile.

## CHAPTER III

## ON LABORATORY TEST

As was mentioned before, some of the literature indicates the fruitlessness of fatigue or corrosion fatigue tests as a means of obtaining engineering data. The author agrees with these ideas for the most part. However certain tests to prove cause and effect may be useful in explaining basic principles.

In this thesis, which attempts to relate internal stress build up with changes in free energy or electro chemical nature, or perhaps entropy, a laboratory test if properly conceived and performed may shed some light on these relationships. In this regard it may be well to indicate a dilemma facing an investigator proceeding in this field.

It is generally accepted that even where there is no cracking, or embrittlement, the presence of static stress may still effect corrosion. 27, 28, 81. This subject has been discussed and frequently referred to in the literature. Examination of the data give a confused picture; some authors have found static stress to increase corrosion, others have found no effect, and still others report a decrease in corrosion.[81] The effect may be specific for both the metal and its environment. Note, the term static stress rules out

a dynamic condition such as the simultaneous effects of corrosion and fatigue. At any rate, the borderlines between corrosion fatigue, stress corrosion cracking, and the effects of stress on general corrosion are not sharp.[81]

## A CORROSION EXPERIMENT

With this outlook, it was decided to attempt a corrosion test to see if it would be possible to determine a series of curves considering the following parameters:

1. Stress
2. Frequency of reversals (say a rotating beam machine)
3. Total number of cycles
4. Corrosion rate

All procedure was considered in the light of reproducibility to make each run as close as possible to the one preceeding.

The specimen selected was a standard fatigue specimen (see Fig. 1) manufactured by the Ann Arbor Instrument Co., Ann Arbor, Michigan. Hot-rolled 1018 Steel was selected. The specimen was fatigued at constant stress and constant R. P. M. in the R. R. Moore fatigue machine.

After fatiguing, the specimen was corroded in .03N HCl for an average time of 20 hours, at a constant temperature, and the corrosion rate was determined by Gravimetric means. Six corrosion tests were made four of which ~~and~~ are shown plotted in Fig. 2.

Details of the corrosion test are as follows:

1. Temperature control was maintained by means of a Fisher Unitized Constant Temperature Bath (Catalog No. 15-445 Fisher Scientific) Reference 92. The coolant, water was agitated by means of an electric stirrer at all times when a corrosion test was in progress.

2. The specimen was immersed in a 1000 ml Erlenmeyer flask containing 1000 cc of .03N HCl at an average depth of 1-1/2 inches below the surface. It was suspended by means of a nylon cord, with rubber plugs or stoppers in the ends to prevent damage by corrosion to the screw threads.

3. The corrosion medium was aerated by means of a small blower discharging under a head of a few inches of water. The purpose of the aeration was two fold:

a. It served to agitate the solution. This was considered desirable from the standpoint

of reproducibility. Complete stagnant conditions are practically never obtained due to thermal gradients.

b. By bubbling air into the solution it was hoped that it would speed up the cathodic depolarizations thus perhaps make the surface reaction the slowest, thus, controlling one. Aeration would increase the corrosion rate.

4. .03N HC 1 was selected as the corroding medium for this first run since only one specimen was to be used (economy purposes). Only a few runs could be made if other than a mild corroding medium were used. At low corrosion rates, the surface and volume of the specimen can be considered as remaining constant over a longer period of time in corrosion medium.

5. The specimen was degreased in Acetone.

6. The specimen was dried in an oven for 15 minutes at 120°C. Each drying was preceeded by a 5 minute immersion in methyl alcohol.

7. Corrosion products were removed by immersion in boiling .1M di basic Ammonium

Citrate at 100°C for 15 minutes. This proved quite successful in removing the corrosion products.

8. Weighing was accomplished to .0001 grams by means of an analytical balance.

The corrosion rate was determined in inches per year knowing the total weight, the weight loss for a specific time period, and the volume and surface of the specimen. The volume and surface of the specimen were determined by integration.

For any additional information, consult original data sheets enclosed.

## CONCLUSIONS BASED ON THE CORROSION EXPERIMENT

On the basis of the six corrosion fatigue runs on specimen no. 1, the only conclusion that can be drawn is that this method probably will not give sufficient accuracy to measure a small change in the electro potential which is probably of the order of a few millivolts.[81] Some previous experimenters considered a repeatability in laboratory experiments of ± 20% about the best that can be expected in gravimetric analysis. Reference 91 indicated a repeatability of ± 20% in the corrosion of Copper in acid solutions. The measurement in this case was by means of a radio-

active tracer which measured the rate of corroding metal going into solution.

There were some factors that resulted from the use of only one specimen:

1. The surface condition of the specimen as seen by the corrosion medium was different in every run since the surface was being progressively corroded away.

2. The formation of chemically formed knotches is unavoidable. Ideally in the fatigue of a specimen, the surface should be polished to eliminate as much as possible any surface knotches, thus stress concentrations.

3. It is difficult, even with complete immersion, which was used, to get uniform corrosion over the entire specimen. Differential corrosion warps the specimen, thus fatigued severe vibrations can induce shock loads thus departing from pure bending, and making the results nearly impossible to reproduce.

There are some advantages to using only one specimen:

1. It is cheaper

2. There is no variance in the metallurgical content of the specimen from run to run.

One serious drawback in the chemistry of the experiment was the lack of knowledge of the rates of reaction. It is strongly suspected by the author that the controlling i.e. the slowest reaction in this case was either cathodic depolarization.

$$4H + O_2 \longrightarrow 2H_2O$$

or hydrogen gas evolution

$$2H^+ + 2e \longrightarrow H_2 \uparrow$$

rather than the iron going into solution

i.e. $$Fe \longrightarrow Fe^{++} + 2e$$

If the iron going into solution is not the controlling reaction, the corrosion process would be independent of the micro structure.[74, 75] Conversely, in order to determine the variance in the amount of iron going into solution, the reaction at the metal surface must control, i.e. be the slowest. For the case at point, any change in the electro-

chemical behavior of the 1018 mild steel used could not be determined by a corrosion process unless the reaction of the Fe going into solution controlled.

The use of a solution with higher hydrogen iron concentration i.e. a more concentrated solution of HCl would have greatly increased the corrosion rate. This in itself gives indication that the Hydrogen reactions are the controlling ones.

## AN EXPERIMENT TO MEASURE CHANGES IN ELECTRO POTENTIAL

As was discussed previously, changes in the internal energy of a metal should reflect changes in the free energy of the metal. This change in free energy should exhibit itself by changes in the electropotential of the metal in solution.

As far as corrosion fatigue is concerned, an increase in electropotential of the metal in solution would indicate a more rapid corrosion rate due to the internal energy build up. If it would be possible to relate internal energy build up to changes in electropotential, it would be helpful in explaining the visual evidence of increased corrosion rate near weld, punched holes, and other areas of internal residual stress.

Briefly, an experiment was devised where the electro-

potential of a series of steel specimens were obtained in .03 N HCl solution in reference to a standard saturated calomel electrode before and after cyclic stressing. Cyclic stressing was accomplished by means of a Calidyne Shaker system model 219. This shaker works in the audio range.

The decision to use this type of stressing system was made for the following reasons:

1. A stressing system which could give a high degree of reproducibility was sought.

2. The high frequencies available considerably shortens the stressing time over the Olsen machine used in the corrosion experiment.

3. Record of the strain cycle could be recorded in an oscilloscope.

4. It seemed that this system would provide a better source of internal residual energy since the stress was in one direction only i.e. the specimen was always in compression and cycled between limits of compressive stress.

There were certain problems that evolved when the decision was made to utilize the Calidyne shaker for the purpose of building up internal stress. The limit of the machine is 20 g. That is, the maximum force available to stress the specimen is twenty times the weight of the specimen. Higher mathematics is not needed to see that this stress level would be much too low to produce any appreciable effect. It was then decided to go to a small specimen and put it under compression by means of a large weight which could be bolted to the shaker table. The use of a large weight when acted on by the 20 g. force compressing a small specimen could induce stresses near the compressive yield point of the material. The use of bolts, outside of their need to hold the weight in place, also provided a means of applying an additional initial compressive stress.

Specimens 1/4" in diameter 1/4" high in the shape of a right circular cylinder were used. A 20 pound weight was used. This weight was held in place by four bolts. Tension in the bolts was controlled by means of a torque wrench. It was impossible to get the tensile stress in the bolts by means of a torque wrench. The wrench was used primarily to distribute the load evenly over the four bolts. Had time permitted, a better solution would have been to put

strain gages on the bolts and thus get a measure of the initial compressive stress level on the specimens.

Runs were made at near constant frequency of 1034 C. P. S. and near constant stress over the range of $10^6$ to $10^8$ cycles. Any value of stress given would be a guess since, as was mentioned previously, the initial tension in the bolts was not known. It is known that the stress did exceed the elastic limit however, since plastic deformation in the specimens did take place.

Accelerometers were placed on the shaker table and on the top of the weight to ascertain if a force of 20 g was being developed. These accelerometers also would indicate if there was any differential movement between the weight and the table. There was. See photograph of Lissajous figures taken at various time intervals during the test. The upper curve is the output of the accelerometer on the 20 pound weight. The lower curve is the output of the accelerometer on the shaker table. It is seen that such an arrangement is useful in repeating a strain cycle.

Electropotential measurements, before and after stressing, were made in .03 N HCl solution with the specimen and solution forming one half cell and a standard saturated calomel reference cell forming the other half cell. The difference in potential between the electrodes was measured

by a Rubicon potentiometer. As soon as an electric circuit was made, a stop watch was pushed, and a series of voltage readings were taken over a period of time. Thus a polarization curve was established.

A jig, to hold the specimen in solution while electropotential measurements were made, which would be out of contact with the electrolyte, was necessary. A rubber sleeve was used which slipped over the specimen making a tight seal. Within this rubber sleeve was a spring loaded contact which completed the electric circuit to the specimen. Thus, the electrical contact was isolated from the electrolyte. When a series of reading was completed, the specimen was reversed in the rubber sleeve, and electropotential readings were taken on the other end of the specimen.

By taking the reading before and after stressing and on both ends, a total of four groups of readings were taken on one specimen. Four specimens were used, each cut off the same rod to insure as much as possible, similar metallurgical structure. The results are plotted on Figs. (5 through 12)

It was realized prior to the experiment that one of the greatest sources of error would be the fact that bulk measurements were used to measure a very localized effect. Thus, if there was any stress relief due to the cyclic

strain any lower potential may tend to offset any increase in potential caused by internal residual energy build up. It was also realized that the potential measured would only be affected by whatever change took place at the surface. It could only be assumed that the effect at the surface was representative of the entire specimen. Since cyclic axially compressive stress was utilized this is probably a more valid assumption than if surface grinding or reversed bending were used.

## CONCLUSIONS DRAWN FROM THE EXPERIMENT

The results were consistant in direction only. In each case, a decrease in electropotential was experienced when comparing the stressed specimen to the unstressed specimen. On the basis of these four specimens, no correlation can be made between the amount of cold work, and the change in potential. It is seen that the maximum potential difference after 18 minutes occurred in specimen no. 1 end no. 2. This was .04 volts, or a decrease in potential of 7.25%. The minimum potential difference was experienced with specimen no. 2 (both ends) where a decrease in potential of about 1% was recorded. The average decrease in potential was 3%.

As is seen, specimens 3 and 4 exhibited excellent consistancy when the ends of the specimen were reversed. This consistency held for both the stressed and unstressed

condition. In specimens 1 and 2, a difference somewhat less than 1% was recorded between the two ends of the specimen. Note that these percentages refer to the voltage readings when polarization was completed. The slopes of the curve are another matter.

While in each case the slope of the curve in the stressed and unstressed condition varied slightly indicating that in general the rate of polarization was slightly less on the stressed specimen, no particular significance is attached to this observation. The difference was not great in any of the cases.

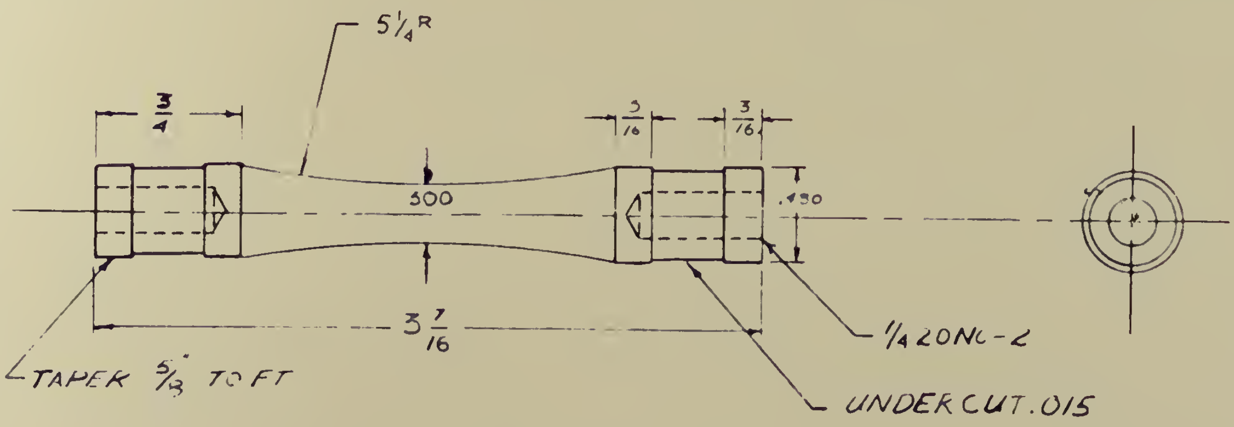
The results were unexpected. Where a slight increase in potential was predicted, a consistant decrease in potential was realized. The magnitude of the change however neither supports nor completely rejects the theory that latent energy build up can increase the chemical activity of a metal.

As was mentioned before, bulk measurements may not reflect very localized changes in potential. On a microscopic scale, differences in potential may be set up as a result of plastic deformation which may result in a high rate of localized pitting. Bulk or average measurement would not accurately reflect these localized peaks in potential.

Annealed specimens were not used. Since the previous history of the specimens was unknown, it is possible that the input of energy by means of the Calidyne shaker was small when compared with previous cold work the specimen may have received. In such a case, the additional cycling may have served as a means of stress relief, thus decreasing the latent energy. The specimens were cut from a 1/4" rod. It is reasonable to assume the rod did receive a fair amount of cold work in a forming operation. Generally when a metal has been cold worked, its surface is in tension. Thus the internal stress build up, at least as seen by the surface would be somewhat compensated for by axial compressive stress cycles.

The use of annealed specimens would have been better. The time and the equipment were not available to accomplish annealing of the specimens.

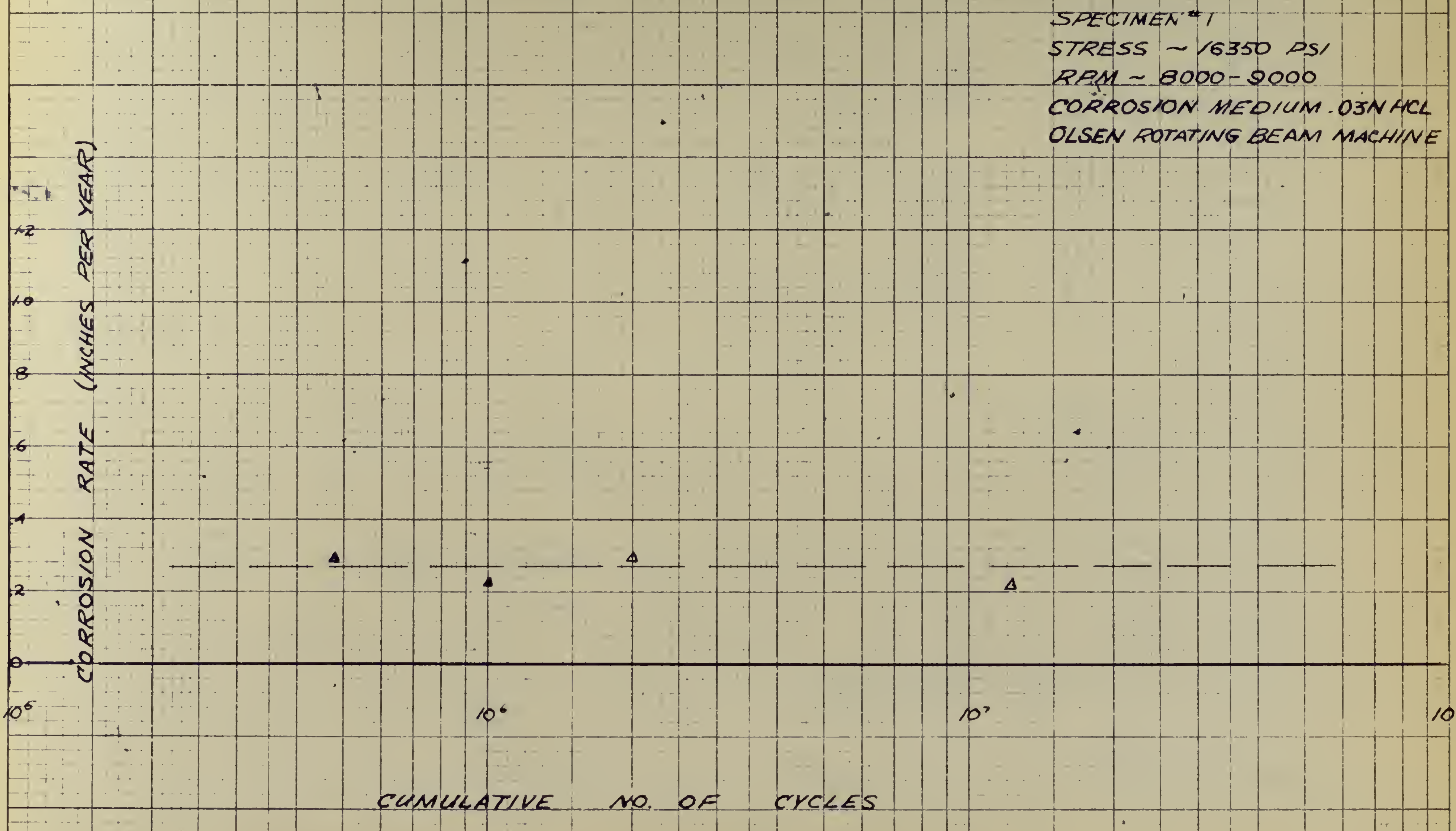
A better approach would be to measure the electropotentials on a much smaller scale. Perhaps even down to the individual crystals if specimen of fairly large crystal size were available. Measuring electropotentials does have merit in that it should give a direct measure of chemical activity thus corrosion rate. Severe experimental problems result when trying to measure fairly small electropotentials over microscopic areas.




STANDARD FATIGUE SPECIMEN

SCALE ~ FULL

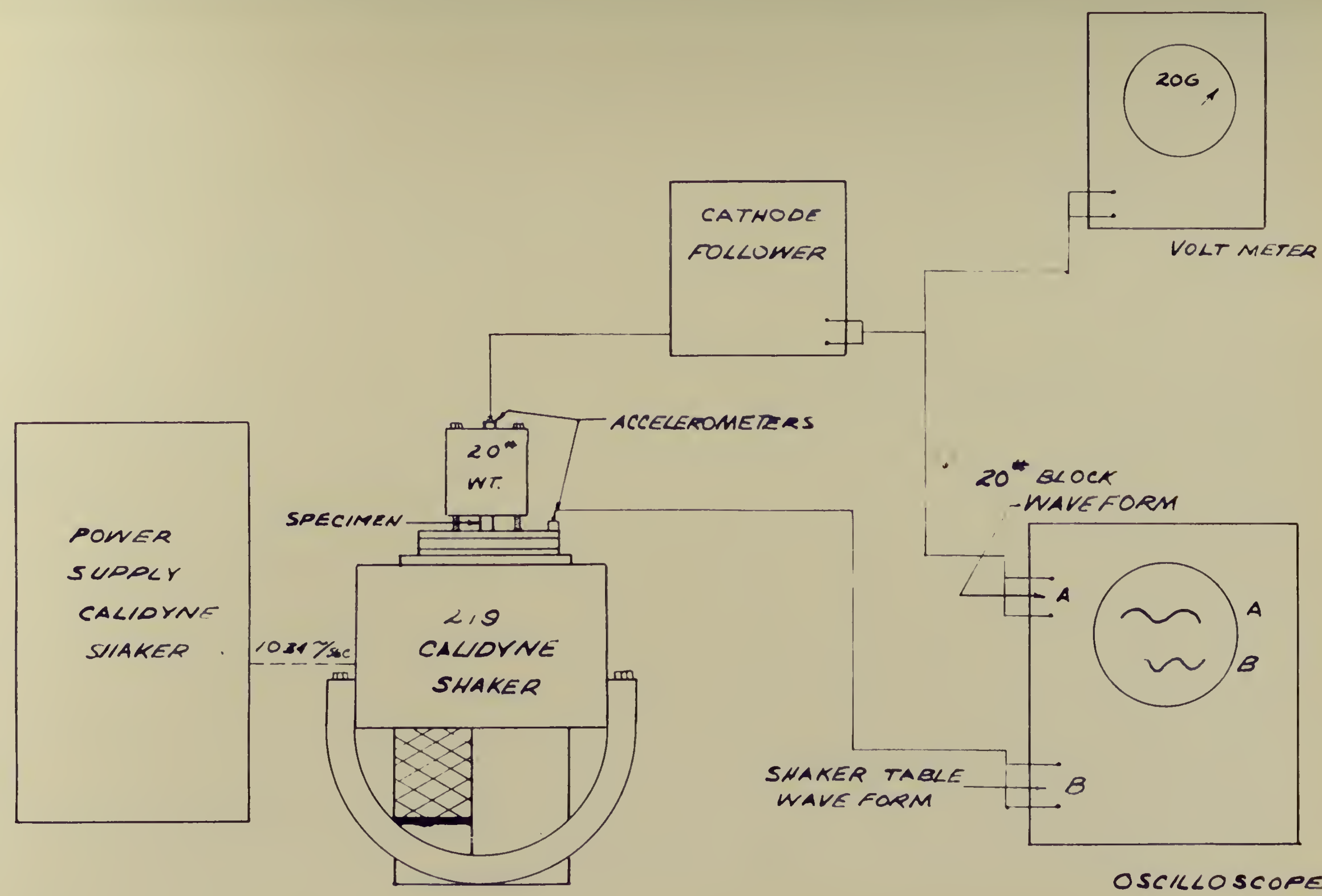
FIG - 1



SPECIMEN #1
STRESS ~ 16350 PSI
RPM ~ 8000-9000
CORROSION MEDIUM .03N HCL
OLSEN ROTATING BEAM MACHINE
CORROSION RATE (INCHES PER YEAR)
1.2
1.0
.8
.6
.4
.2
0
$10^5$
$10^6$
$10^7$
$10^8$
CUMULATIVE NO. OF CYCLES


FIG - 2

R.D.B. 60




LABORATORY SETUP FOR CYCLIC STRESSING WITH CALIDYNE SHAKER

R.D. BIEDERMAN MAY '60

FIG 3

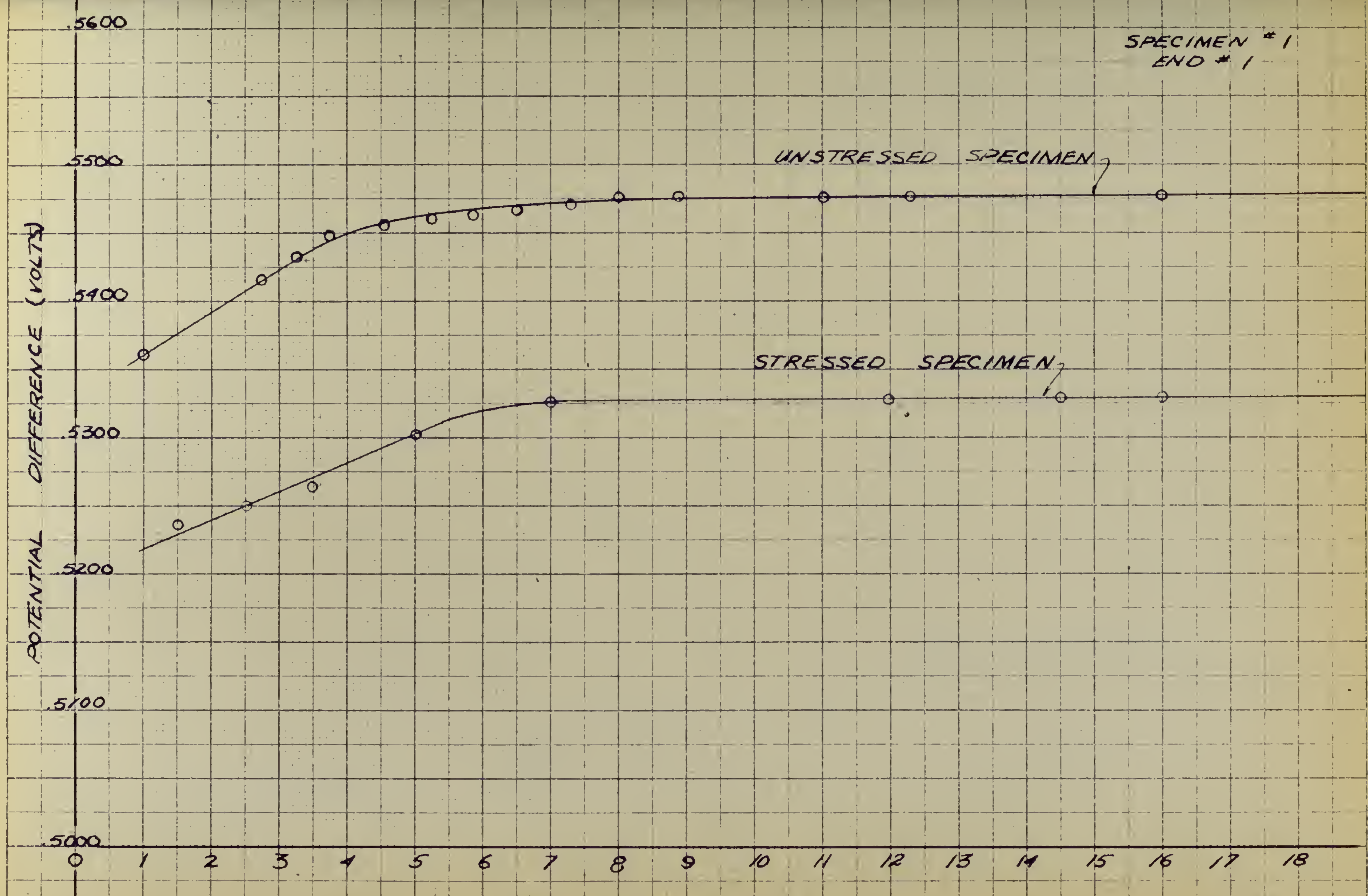

SPECIMEN #1
END #1
UNSTRESSED SPECIMEN
STRESSED SPECIMEN
.5600
.5500
.5400
.5300
.5200
.5100
.5000
POTENTIAL DIFFERENCE (VOLTS)
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
TIME (MINUTES)

FIG. 5

R.D.B. '60

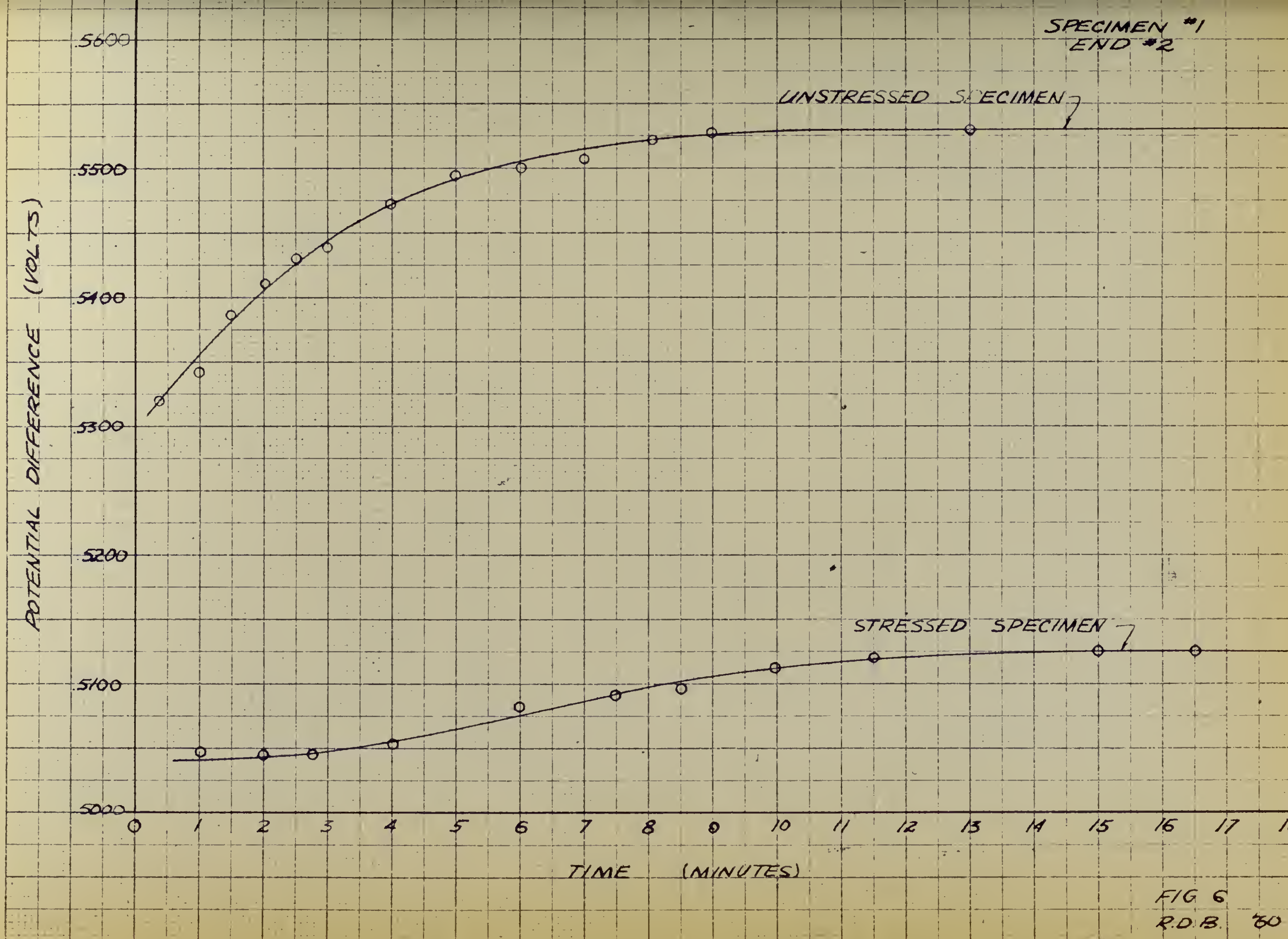

SPECIMEN #1
END #2
UNSTRESSED SPECIMEN
STRESSED SPECIMEN
.5600
.5500
.5400
.5300
.5200
.5100
.5000
POTENTIAL DIFFERENCE (VOLTS)
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
TIME (MINUTES)

FIG 6
R.D.B. '60

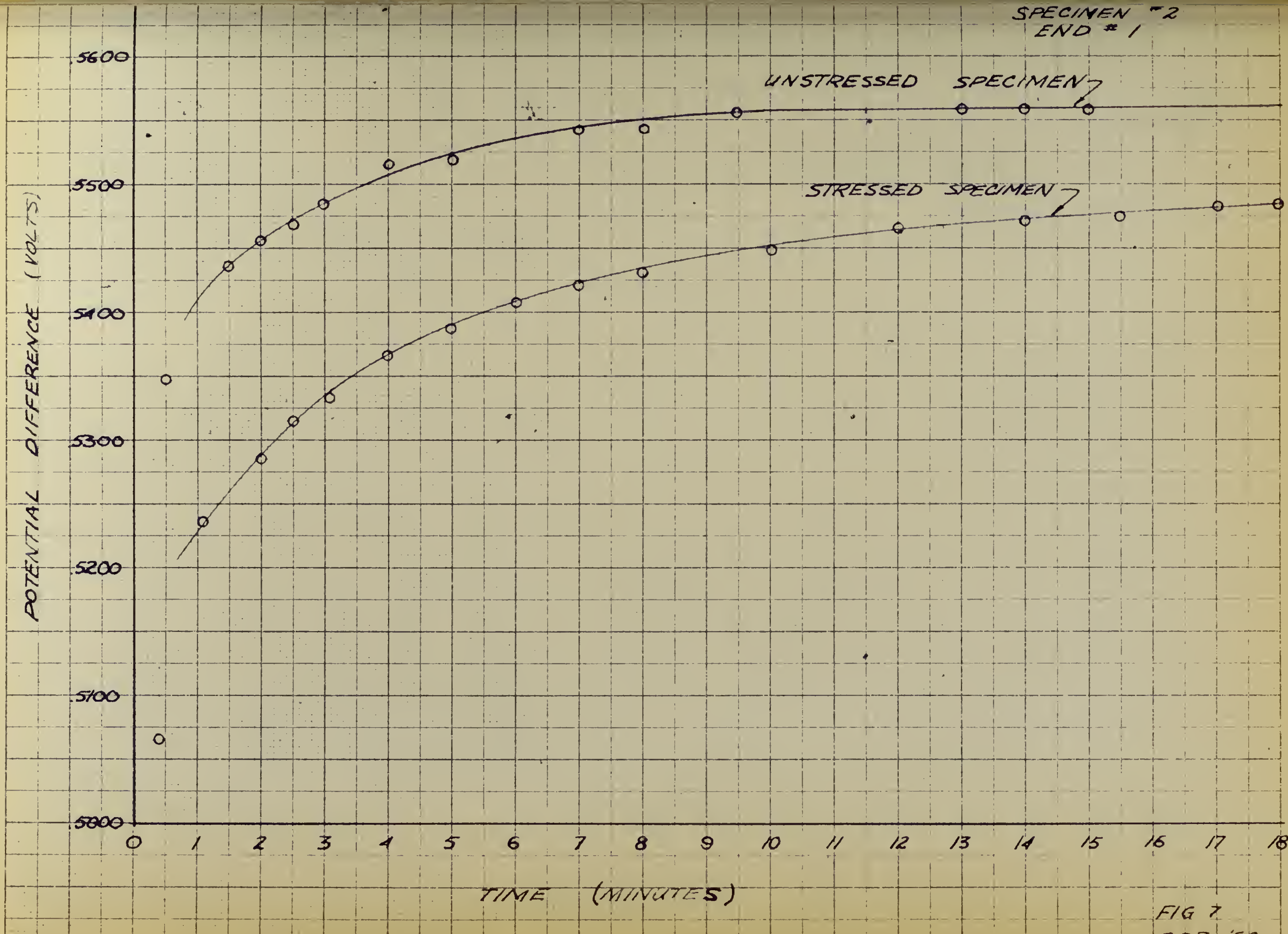

SPECIMEN #2
END # 1
UNSTRESSED SPECIMEN
STRESSED SPECIMEN
5600
5500
5400
5300
5200
5100
5000
POTENTIAL DIFFERENCE (VOLTS)
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18
TIME (MINUTES)

FIG 7
R.D.B. '60

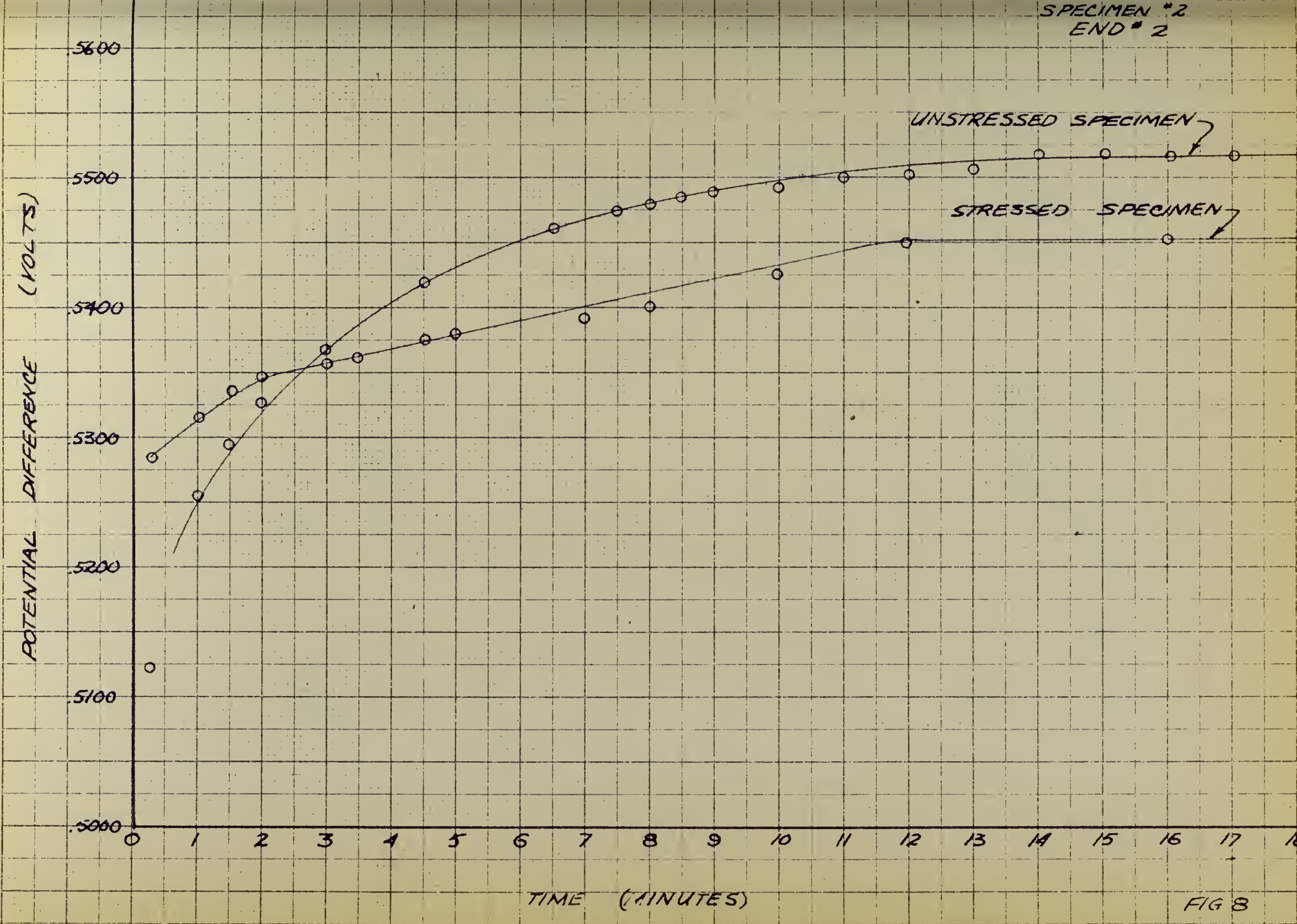

SPECIMEN #2
END # 2
UNSTRESSED SPECIMEN
STRESSED SPECIMEN
POTENTIAL DIFFERENCE (VOLTS)
.5600
.5500
.5400
.5300
.5200
.5100
.5000
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
TIME (MINUTES)

FIG 8
R.D.B '60

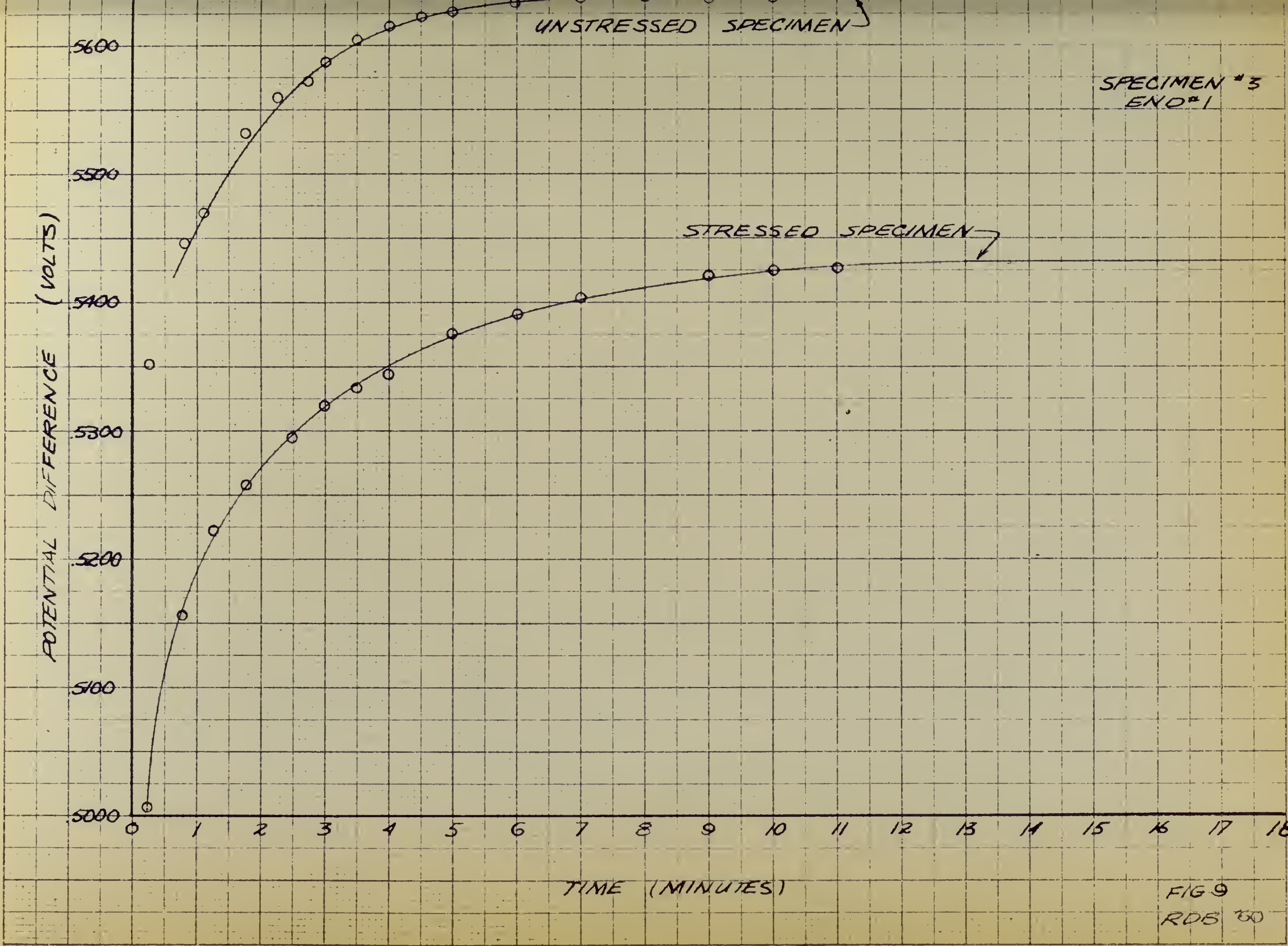
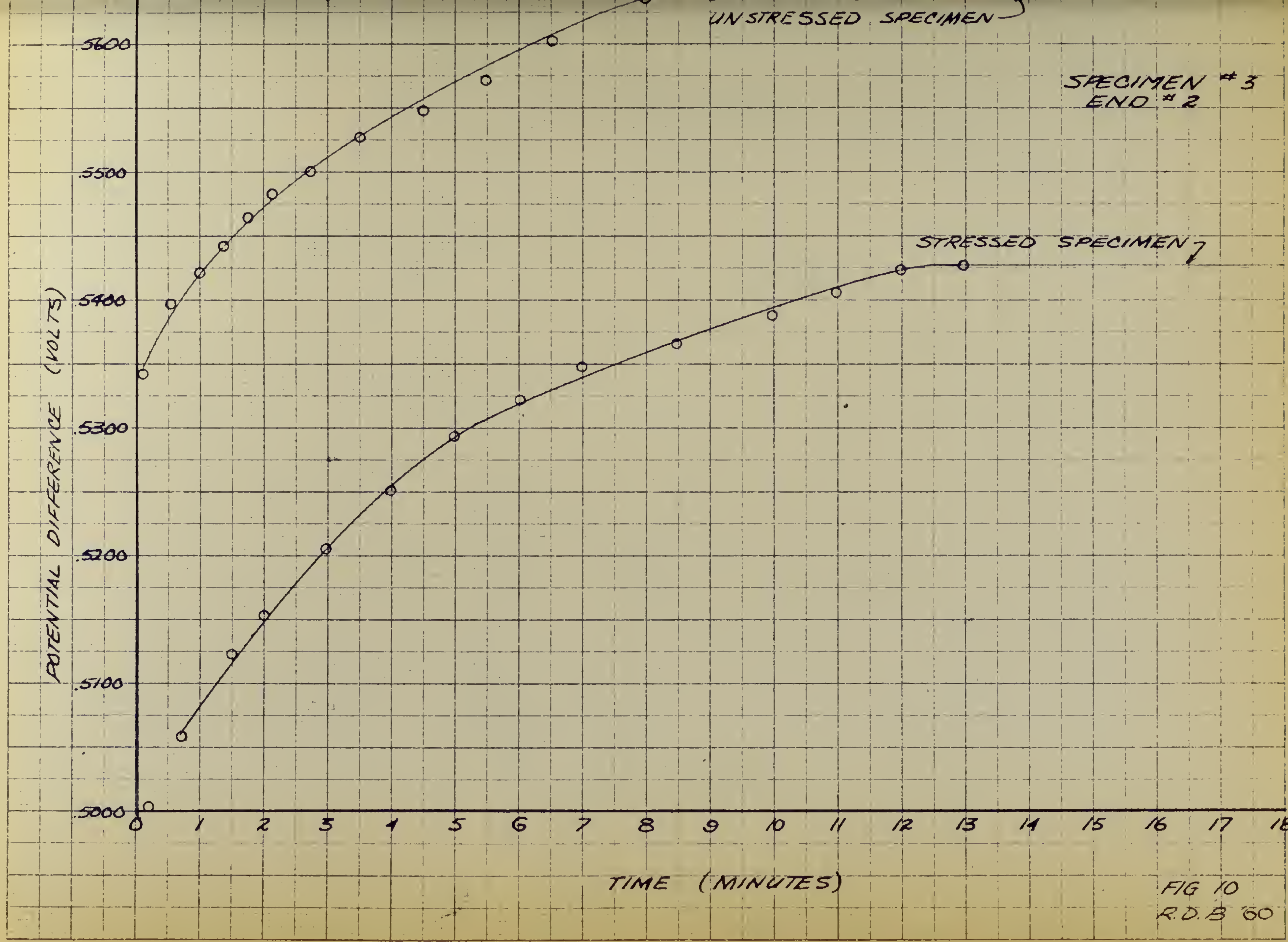

UNSTRESSED SPECIMEN
STRESSED SPECIMEN
SPECIMEN #3
END #1
POTENTIAL DIFFERENCE (VOLTS)
5600
5500
5400
5300
5200
5100
5000
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
TIME (MINUTES)

FIG 9
RDS '60



UNSTRESSED SPECIMEN
SPECIMEN #3
END #2
STRESSED SPECIMEN
.5600
.5500
.5400
.5300
.5200
.5100
.5000
POTENTIAL DIFFERENCE (VOLTS)
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
TIME (MINUTES)


FIG 10
R.D.B '60

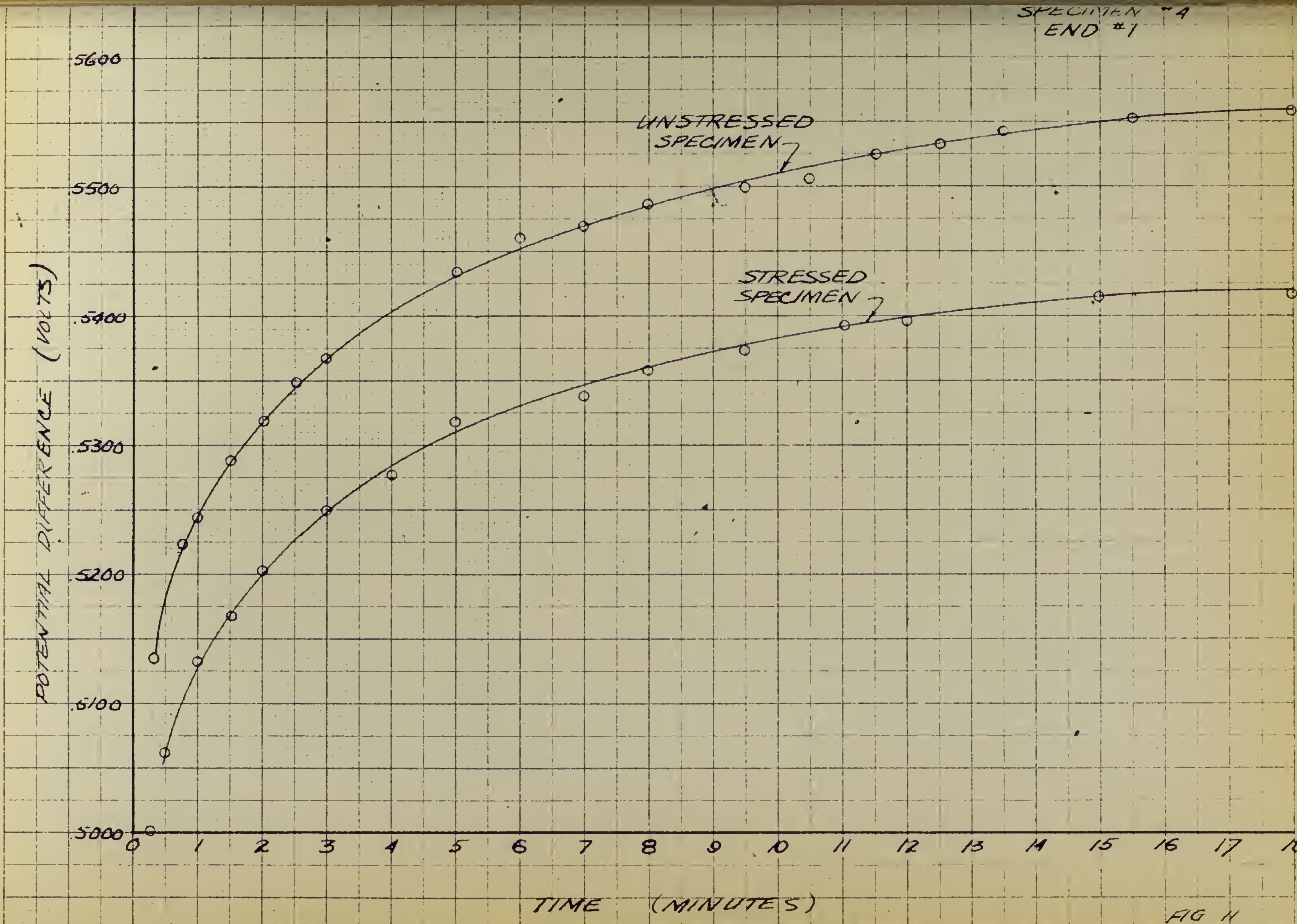
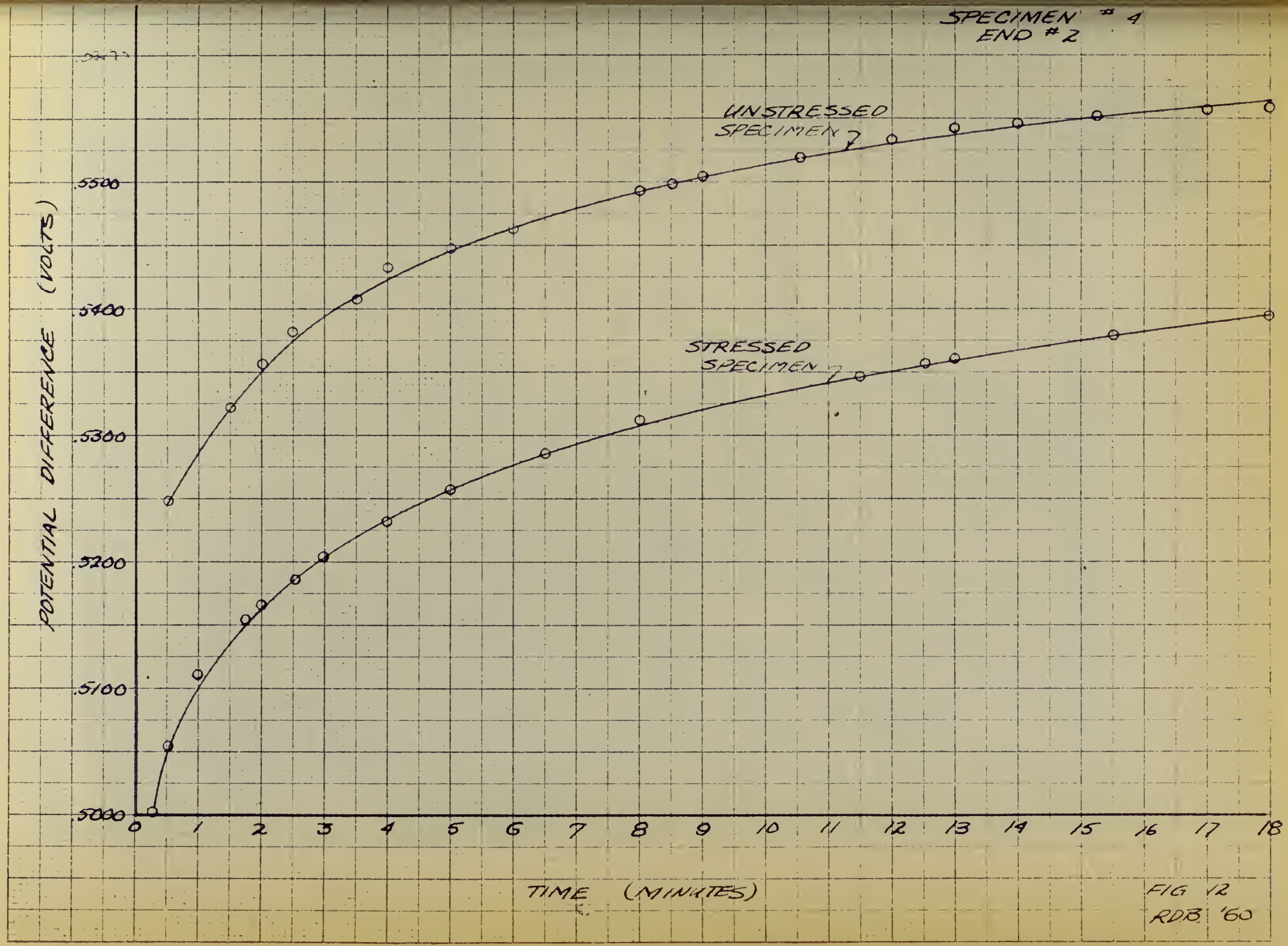
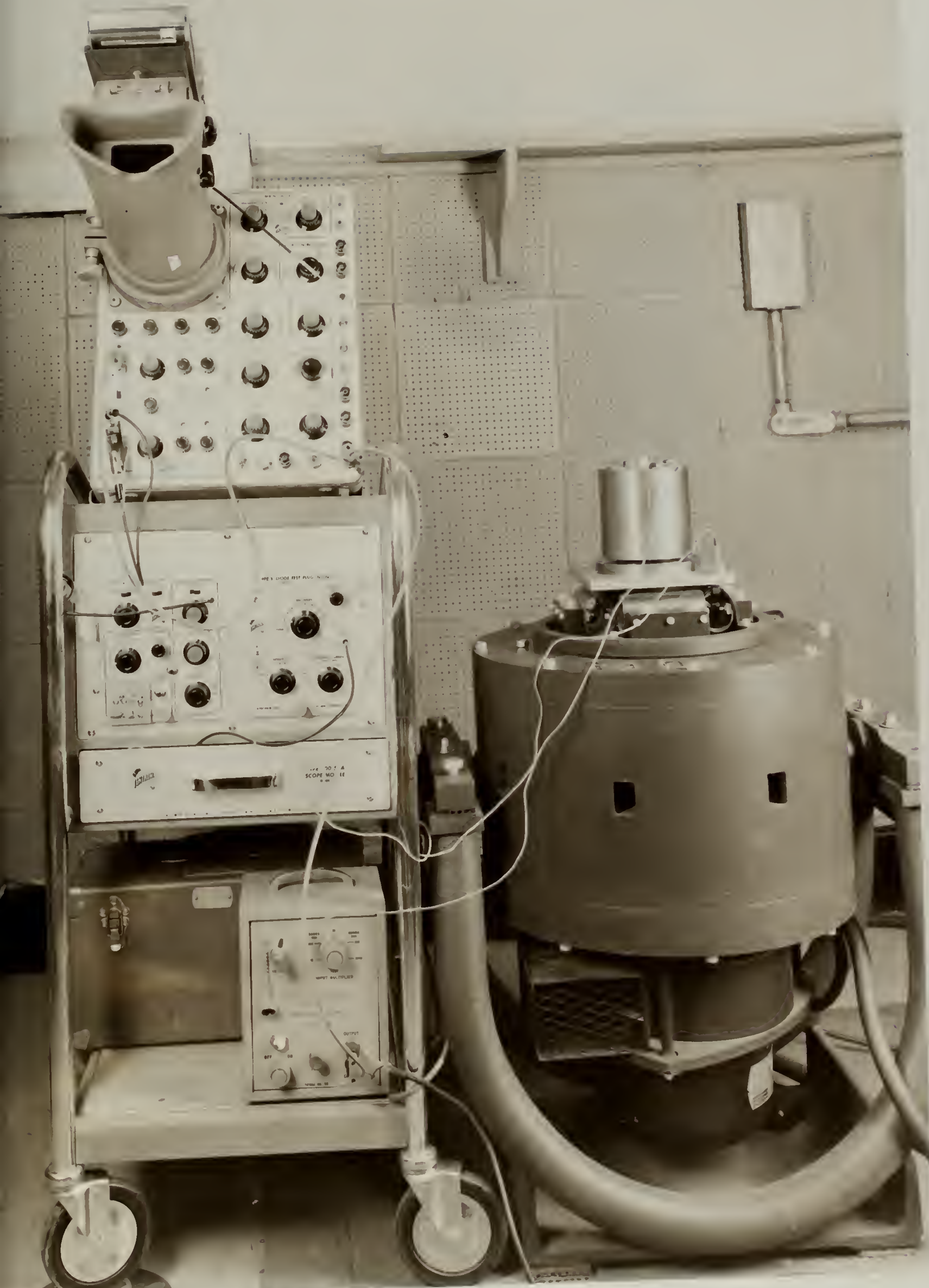

SPECIMEN #4
END #1
UNSTRESSED SPECIMEN
STRESSED SPECIMEN
.5600
.5500
.5400
.5300
.5200
.5100
.5000
POTENTIAL DIFFERENCE (VOLTS)
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18
TIME (MINUTES)

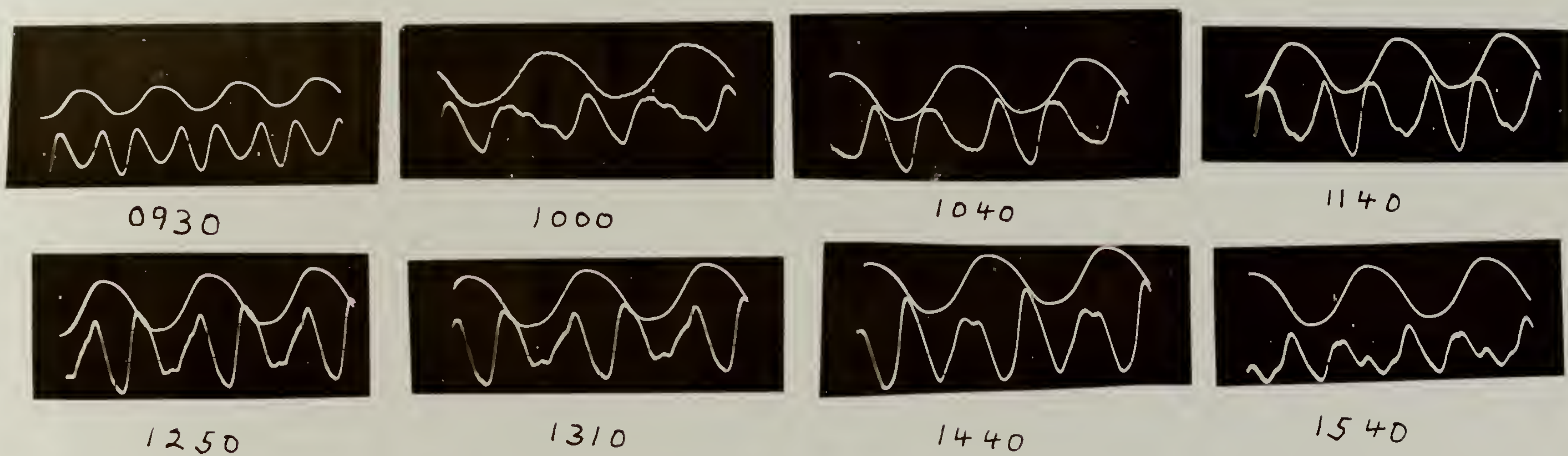
FIG 11
R.D.B. '60


SPECIMEN # 4
END # 2
UNSTRESSED SPECIMEN
STRESSED SPECIMEN
POTENTIAL DIFFERENCE (VOLTS)
.5000
.5100
.5200
.5300
.5400
.5500
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
TIME (MINUTES)
FIG 12
RDB '60



LABORATORY SETUP USING CALIDYNE SHAKER SYSTEM

FIG 3A




PHOTOGRAPHS OF LISSAJOUS FIGURES
SPECIMEN NO. 4

FIG 4

# CHAPTER IV

## TOWARD FUTURE WORK

The major portion of the literature study and the laboratory work was done in search of a feasible way of measuring internal stress or latent energy build up and, if possible, to determine the effect this latent energy build up has on other mechanical properties of a metal. These purposes are complementary since any change in mechanical properties may provide a means of evaluating the stored or latent energy.

The limitations of the methods tried in the laboratory work were brought out in Chapter III. In the course of the work, two other methods seemed to have promise and worthy of additional work. The use of a calorimeter and differential temperature thermocouple briefly discussed in Chapter II seem to possess many advantages and few of the disadvantages of the methods tried. These methods measure the release of the stored energy. The effect of this stored energy on mechanical properties would have to be determined from another experiment.

These methods also plague the investigator with the experimental difficulty of accurately measuring small quantities.

Some investigators differ in their analyses as to when,

on the temperature scale, this release takes place. This involves careful plotting of results as the specimen is being annealed. The use of automatic recording equipment is a practical necessity.

The calibration of a calorimeter to measure such small differences is a sizable task. The big advantage is that the calorimeter provides a non-destructive means of measuring internal energy release. Differential temperature measurements have the difficulty of correlation between the temperature measurements and the energy to obtain the internal energy release. The readings should reflect changes in the internal, (i.e. not just at the surface) structure of the specimen thus should give a more accurate indication quantatively of the energy released.

## NEW IDEAS ON FATIGUE

The need for research in fatigue strength of metal is becoming more apparent in regards to deeply submerged submarines. The concept of the fatigue test and the value of the S/N curve are being looked at from a different aspect. Previously, structures were designed primarily such that the design load was below the "fatigue strength" of a metal. Thus, the piece was designed to be able to withstand $10^7$ or more cycles.

This is really not feasible nor necessary in designing the hull of a submarine capable of deep submergence. In

its lifetime, no submarine will cycle her hull from zero submergence to operating depth $10^7$ times. Thus, much greater emphasis is placed on the part of the curve to the "left" of the knee. That is, operating at a cyclic stress greater than the fatigue strength, how many cycles can the hull withstand? Should depth limitations, based on fatigue, be imposed after so many years of service?

The frequency of cycling has also come under review. Low cycle fatigue tests are being conceived to laboratory test the materials. Previously, high frequency of cycling was used primarily to reduce the time of the fatigue test. Much new data is needed in this "unsafe" range with the cycling frequency of stress down to perhaps 6 stress cycles per hour. This newer concept, along with the more exotic metals used in construction, has frequently left the laboratory investigator considerably farther behind the engineers who are seeking criteria on which to base scantlings for construction.

There does not seem to be any lack of possible roads to travel in this area of basic research, rather, experimental difficulties in laboratory tests have provided the limitations.

In the meantime, laboratory tests will continue in an effort to explain the basic process of corrosion fatigue. Perhaps when these experimental results can be supported by

theory, the end of experimental work will be in sight - for then, a selection of an alloy to do a specific job can be made from theoretical considerations alone. This will generally result in a considerable saving in time and money.

As in many other fields, the problem of randomness, in this case in the crystal structure, must be dealt with. Statistics provide an approach, but definitely not a complete answer. Reference 131 is a fairly recent example of approaches at representing dislocations in crystal lattice. However, before any confidence can be placed in these presentations, it must be proved that the mathematical model is a valid representation of what exists in a crystalline material. But, this is another area in which there is no lack of possible roads in which to pursue understanding.

## APPENDIX

The deformation of a body can be analyzed by the First Law of Thermodynamics.

$$\Delta E = Q + W \qquad (1)$$

Where: $\Delta E$ is the change in internal energy of the body

$Q$ is the heat effect associated with the deformation (+ if absorbed)

$W$ is the work (+ if done on the body)

For analysis by the First Law of Thermodynamics, a process need not be carried out in a specific manner, such as isothermally or adiabatically. Thermodynamic reversibility is not a necessary condition, thus this can be applied to both elastic and plastic deformation.[140]

Some methods for measuring latent or stored energy determine the change in heat content or enthalpy $\Delta H$

at constant pressure:

$$\Delta H = \Delta E + P\Delta V \qquad (2)$$

Where: $P$ Hydrostatic pressure

$\Delta V$ the volume change associated with the process

$\Delta E$ internal energy

Note that in this equation, $P \Delta V$ is negligably

small for solids at or near atmospheric pressure.

Then:

$\Delta H = \Delta E = Es$ (3) Where $Es$ = the stored or latent energy.

It is desirable to measure changes in entropy if changes in free energy are sought.

$$\Delta S \qquad \frac{Q\ rev}{T} \qquad (4)$$

Where: $\Delta S$ Change in Entropy

$Qrev$ heat for a reversable process only

$T$ temperature

Since the cold worked state of a metal cannot be reached by any reversible path, the entropy change cannot be evaluated by this equation.

The Gibbs free energy, G is related to other thermodynamic changes by the equation:

$$\Delta G = \Delta H - T\Delta S \qquad (5)$$

from (3) $\Delta G \approx \Delta E - T\Delta S$

But there is still the problem of determining $\Delta S$. $\Delta S$ cannot be determined by (4) since the cold work process is not rever-

sible.

Electrochemical measurements seem attractive since:

$$\Delta G = - n F E \qquad (6)$$

Where:

| | |
|---|---|
| $\Delta G$ | Change in free energy |
| $n$ | the valence of the active ion |
| $E$ | the open circuit potential of the reversible cell |
| $F$ | Faradays' constant |

Note that a reversible cell must be formed. A cell composed of a cold worked and annealed specimen is not a reversible cell. Measuring the potential in reference to a saturated calomel cell provides a reversible cell for all practical considerations.

Thus, there is a theoretical background for determining changes in free energy with changes in electropotential. However, the practical experimental difficulties, as presented in Chapter III, must be overcome if useful information is to be obtained by this method.

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